ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

PRODUCTION OF FIBER REINFORCED THERMOPLASTIC COMPOSITES

Ph.D. THESIS

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Department of Polymer Science and Technology

Polymer Science and Technology Programme

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

ELYAF TAKVİYELİ TERMOPLASTİK KOMPOZİTLERİN ÜRETİMİ

DOKTORA TEZİ

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Polimer Bilim ve Teknolojisi Anabilim Dalı

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EKİM 2012

Gülnur Başer, **a Ph.D.** student of ITU **Graduate School of Science Engineering and Technology** student ID **515062003**, successfully defended the **thesis** entitled **PRODUCTION OF FIBER REINFORCED THERMOPLASTIC COMPOSITES**", which she prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

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FOREWORD

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Chemical Engineer

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ABBREVIATIONS

TP	**:**Thermoplastic
CBT	**:**Cylic buthyleneterephtalate
IPCBT	**:**In situ polymerized cyclic buthyleneterephtalate
PBT	**:**Poly buthyleneterephtalate
PA12	**:**Polyamide 12
CoPA	**:**Copolyamide
RTM	**:**Resin transfer molding
NCGF	**:**Non crimp glass fFabric
CFRPCs	**:**Continuous fiber reinforced polymeric composites
PP	**:**Polypropylene
PA	**:**Polyamide
PET	**:**Poly ethylene terephtalate
FRP	**:**Fiber reinforced plastics
PAN	**:**Polyacrylonitrile
ROP	**:**Ring opening polymerisation
APLC-12	**:**Anionicly polymerised lactam12
CDP	**:**Cyclo-depolymerisation
MW	**:**Molecular weight
IPCBT	**:**Insitu polymerised CBT
UD	**:**Uni directional
V_f	**:**Fiber volume fraction
DSC	**:**Differential scanning calorimeter
T_c	**:**Crystallization temperature
X_c	**:**Crystallization degree
SEM	**:**Scanning electron microscopy
VE	**:**Vinyl ester

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PRODUCTION OF FIBER REINFORCED THERMOPLASTIC COMPOSITES

SUMMARY

In structural polymeric composite applications, textiles (e.g., unidirectional, woven fabrics) are commonly used for reinforcement because of two reasons: high fiber volume fraction and the possibility to tailor the load bearing capacity through the fiber lay-up. The thermoset resins are predominantly in use as matrix materials in textile reinforced composites due to their easy processability and enhanced fiber wetting capability. Although they can be processed easily, they contain organic volatiles that damage environment and human health. Furthermore, recycling of thermoset resins are not possible because they cannot be melted upon application of heat for re-molding.

The use of thermoplastic (TP) polymers as matrix materials offers a solution to these particular problems since they are recyclable and environment friendly. They have also high toughness and impact resistance. However, manufacturing high quality thermoplastic composite parts still remain as a problem because of inherent high melt viscosity of many of TP polymers which causes poor fiber impregnation. Conventional thermoplastic processing methods like extrusion and injection molding enables the use of chopped fiber reinforcements from usual blend-process-cast point of view to manufacture composite parts with low fiber volume fractions efficiently. The main limitation for processing however occurs in the case of structural continuous fiber (textile) reinforced composite manufacturing processes where the high melt viscosity problem usually necessitates high pressure applications in order to have good fiber wetting and high fiber volume fractions. Such applications automatically cause increased manufacturing costs.

Fiber impregnation problem may be handled either using methods which decrease the polymer viscosity or reducing the required flow length of polymer matrix. Another approach that is specifically applicable for thermoplastic polymers is the reactive processing of textile fiber-reinforced thermoplastics based on impregnation of the fibers with a low viscosity oligomeric precursor, followed by in situ polymerization. Cyclic butylene terephtalate (CBT), as precursor, has well been studied for this manufacturing approach due to its low melt viscosity. In all applications of this manufacturing approach, the precursor impregnation has been handled via conventional manufacturing techniques such as resin transfer moulding (RTM) which is followed by an isothermal heating. This leads to entropically driven ring opening polymerization resulting in linear high molecular weight matrix polymer. Although TP composite materials may be manufactured using that approach, on an industrial scale, it requires lots of time and poses process difficulties necessitating special equipments.

Yet, it has also been shown that these problems may be eliminated by using properly prepared prepreg materials which also enables the manufacturing of complex shaped end products rather than laminates. Based on this idea, this thesis focuses on the manufacturing of textile reinforced TP composites with new manufacturing methods. Non-crimped E-glass fiber (NCGF) textiles were used as the textile reinforcement. Cyclic butyleneterephtalate (CBT) which is the oligomer of

polybutyleneterephtalate (PBT) was one of the resins used as the matrix of composite. NCGF textiles were coated with CBT/polymerization catalyst mixture via powder scattering method to obtain prepregs. For the preparation of prepregs, first NCGF textile was impregnated with the CoPA suspension and was coated by sprinkling PA12 powder. In situ polymerized CBT (IPCBT) composites and PA matrix composites were produced from prepregs by compression molding in hot press. Composite laminates obtained were subjected to tensile, flexural and impact tests. Optimum process parameters which have to be used in hot press were determined for all types of the matrix resins.

The efficiency of the new manufacturing method for IPCBT composites was sought via performance comparisons with reported literature values and with effective microscopic investigation by scanning electron microscopy (SEM) and stereo microscope. Conventional PBT matrix composites out of commingled PBT/Glass NCGF fabric were also produced by compression molding and compared with IPCBT composites. Moreover, IPCBT composites were produced via vacuum molding out of CBT prepregs and compared with IPCBT composites produced by compression molding.

Detailed performance investigation was carried out by determining the Tsai-Wu strength parameters (X, X', Y, Y', S) of unidirectional IPCBT composite laminates through tensile and compressive tests at longitudinal and transverse directions as well as tensile test of $(+45/-45)_{6s}$ laminates. Test results were compared with the results of simultaneously manufactured and tested NCGF reinforced vinylester (VE) laminates. Failure envelopes of both IPCBT and VE composites were evaluated. Overall, the pros and cons of IPCBT composites manufactured via newly initiated manufacturing method was evaluated and reported.

Figure 1 and 2 corresponds to the first ply failure envelopes of UD laminates where the competitive design space of IPCBT composite laminates was demonstrated in the shaded region. Investigation of the test results and failure modes in accordance with the failure envelopes suggested that the IPCBT based laminates considered in this study can be strong alternatives to the VE based laminates especially under uniaxial compressive loading conditions as well as under impact loadings.

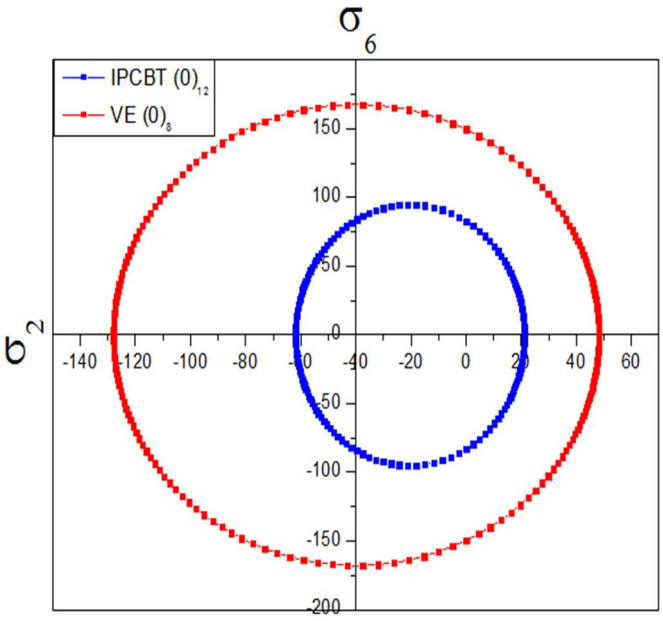


Figure 1 : Failure envelopes of IPCBT and VE Composites on σ_2-σ_6 spaces.

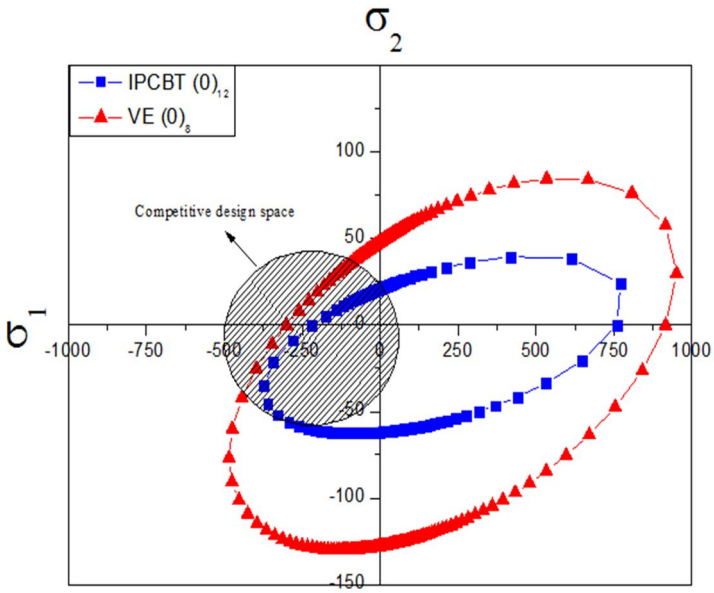


Figure 2 : Failure envelopes of IPCBT and VE Composites on σ_1-σ_2 spaces.

In conclusion, NCGF reinforced IPCBT composites were successfully produced. First of all, optimum prepreg and composite production conditions of IPCBT composites were identified. It was shown that biaxial NCGF reinforced IPCBT composites gave better flexural and tensile properties when it was compared with reported results of IPCBT composites produced by RTM technique and the composites produced by compression molding of conventional PBT in the literature. It was seen that the new method provided reduction in processing time and energy consumption as compared to conventional TP composite manufacturing methods. It was also observed that IPCBT composites can be produced not only by compression molding but also by vacuum molding with an enhancement of both tensile and flexural strengths.

PA matrix composites were successfully produced by compression molding as well. It was observed that the tensile properties of IPCBT composites are higher than those of PA composites.

Sandwich structures of IPCBT composite skin and PA matrix composite skin using PA foam as core material were successfully produced. However, bond strength between skin and core was not enough for both PA and IPCBT. It was concluded that the compression molding in hot press is not a proper method for one-shot sandwich composite production.

ELYAF TAKVİYELİ TERMOPLASTİK KOMPOZİTLERİN ÜRETİMİ

ÖZET

Polimerler hayatımızda çok önemli bir rol oynamaktadırlar. Son kullanım özelliklerine gore farklı polimerler birbirleri ile karıştırılabilir veya farklı yapıdaki malzemelerle birleştirilebilirler. Yapısal polimerik kompozit parçaların üretiminde yük taşıma kapasitelerinin yüksek olması ve yüksek elyaf hacim oranını sağlayabilmelerinden dolayı tekstiller (dokumalar, tek yönlüler vb.) en çok tercih edilen takviye malzemeleridir. Tekstil takviyeli kompozitlerin üretiminde matris olarak çoğunlukla tercih edilen termoset polimerlerin (polyester, epoksi vb.) en büyük avantajı düşük viskoziteye sahip olmaları ve bundan dolayı elyaf takviyeli kompozit üretiminde düşük basınçlarda elyafa kolay tatbik edilebilmeleridir. Termoset reçineler kolay işlenmelerine rağmen insan sağlığına ve çevreye zararlı stiren gibi kolay uçucu çözücü ve çapraz bağlayıcılar içermektedir. Isı ile tekrar eritilip şekil verilemediği için termoset kompozit parçaların geri dönüşümü de mümkün değildir.

Termoplastik (TP) polimerler ise ısıyla tekrar şekil verilebildiği için termosetlerin aksine geri dönüştürülebildikleri gibi insan ve çevreye zarar verecek çözücülerle çalışmayı da gerektirmemektedirler. Ayrıca darbe dayanımları da termosetlere göre daha yüksek olduğundan kompozit uygulamalarında termosetlere alternatif olarak gösterilmektedirler. Ancak, TP polimerlerin eriyik viskozitesi çok yüksek olduğundan iyi bir elyaf emprenyesiyle sağlanabilecek kaliteli bir TP kompozit üretimi hala çözülememiş bir problemdir. Enjeksiyon ve ekstrüzyon yöntemiyle kırpılmış elyaf takviyesi içeren TP kompozitler kolayca üretilebilirken bu kompozitlerin özellikleri birçok kullanım alanında yetersiz kalmaktadır. Çok daha yüksek mukavemete sahip sürekli elyaf (tekstil) takviyeli TP kompozitlerin üretim yöntemleri sınırlı kalmıştır. Çünkü iyi bir elyaf emprenyesi ve yüksek elyaf oranları elde etmek için gerekli yüksek sıcaklık ve basınçlar proses zorluklarına ve maliyet artışına neden olmaktadır.

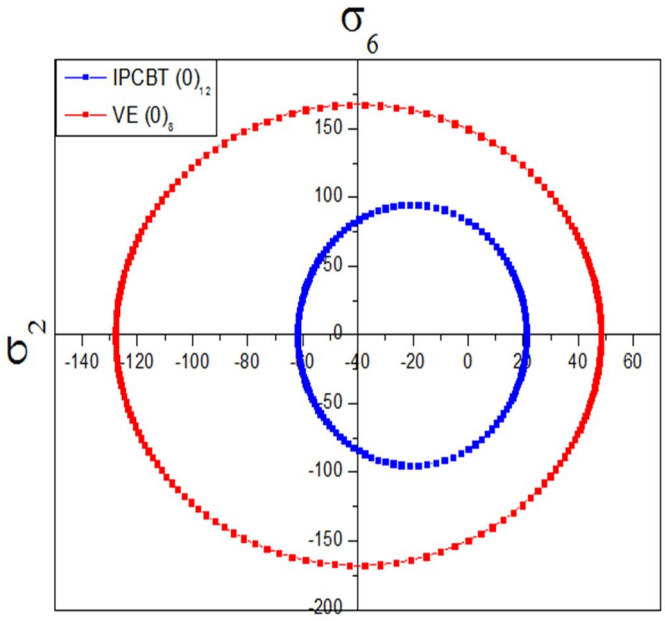
Elyafın TP polimerle ıslatılma problemi polimer viskozitesinin azaltılması veya polimerin akış mesafesinin kısaltılması gibi yöntemlerle çözülebilmektedir. Diğer yöntem ise elyafın düşük viskoziteli oligomerik (veya monomerik) başlangıç maddesi ile emprenye edilip yerinde polimerizasyona tabi tutumasına dayalı reaktif termoplastik polimerizasyon prosesidir ve bu yöntem termoplastik polimerler için uygulanabilen bir yöntemdir. Düşük viskozitesinden dolayı poli bütilen teraftalat (PBT) oligomeri olan halkalı bütilen teraftalat (CBT) bu üretim yönteminde kullanılarak çalışılmıştır. Elyafın oligomerle emprenyesi termoset polimerler için kullanılan geleneksel reçine transferiyle kalıplama (RTM) tekniğiyle gerçekleştirilmiştir. Burada RTM sistemi ısıtılarak izotermal bir prosesle CBT nin polimerleşip lineer ve yüksek molekül ağırlıklı matris polimer olması sağlanmıştır. TP kompozitler bu yöntemle üretiliyor olsa bile endüstriyel boyutta bakıldığında bu sistemin bazı proses zorlukları ve özel ekipmanlara ihtiyaç duyması gibi problemleri ortaya çıkmaktadır. Bahsi geçen problemlerin önceden oligomer (veya monomer) ile emprenye edilmiş tekstillerden (prepreg) kompozit üretilmesiyle çözülebileceği görülmüştür.

Bu çalışma da bu düşünceyi takip ederek yeni yöntemlerle TP kompozit üretimi üzerine yürütülmüştür. Kompozit takviye tekstili olarak kıvrımsız E-camı elyafından (NCGF) tekstiller kullanılmıştır. Kompozit matris polimeri olarak kullanılan polimerlerden biri CBT'dir. Prepreg üretimi, NCGF tekstilinin polimerizasyon katalizörünü de içeren CBT ile toz serpme yöntemiyle kaplanmasıyla gerçekleştirilmiştir. Matris olarak kullanılan diğer reçine poliamiddir (PA). Prepreg eldesi için NCGF tekstili önce kopoliamid (CoPA) süspansiyonuyla emprenye edilmiş, üzerine PA12 tozu serpilerek kaplanmıştır. Yerinde polimerleştirilmiş CBT (IPCBT) ve PA kompozitleri, hazırlanan prepreglerin sıcak preste baskıyla kalıplanması metoduyla üretilmiştir. Elde edilen kompozitler çekme, eğme ve darbe testlerine tabi tutulmuştur. Baskıyla kalıplamada kullanılacak uygun proses değişkenleri her iki matris tipi için de belirlenmiştir.

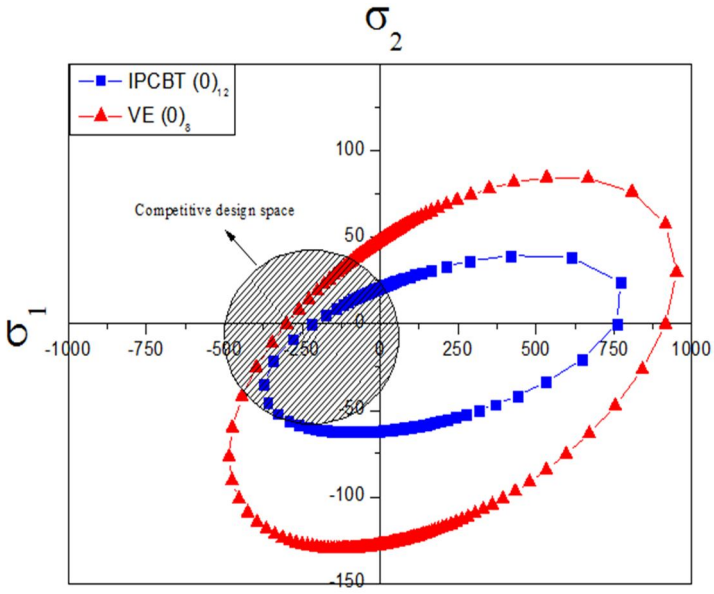
IPCBT kompozitlerinin yeni üretim tekniğinin başarısı literatürdeki mekanik değerlerle karşılaştırma yapılarak ve taramalı elektron mikroskobunda (SEM) yapılan incelemelerle araştırılmıştır. Bilinen PBT matrisli kompozitler PBT/E-camı elyaflarının karışımından oluşan NCGF tekstilinin baskıyla kalıplanması ile elde edilmiştir ve bu kompozitler IPCBT kompozitleriyle kıyaslanmıştır. Ayrıca IPCBT kompozitler prepreglerden vakum kalıplama yöntemiyle de üretilerek sıcak preste üretilen IPCBT kompozitlerin mekanik özellikleri ile karşılaştırılmıştır.

Daha detaylı performans incelemesi baskıyla kalıplama yöntemiyle üretilen tek yönlü (UD) IPCBT kompozitlerinin Tsai-Wu dayanım parametrelerinin (X, X', Y, Y', S) çekme ve basma testleriyle tespit edilmesiyle yürütülmüştür. Test sonuçları eş zamanlı olarak üretilen aynı tür NCGF içeren doymamış vinilester (VE) kompozitlerinin test sonuçlarıyla kıyaslanmıştır. IPCBT ve VE kompozitlerinin kırılma zarfları ve IPCBT kompozitlerinin olumlu ve olumsuz yönleri değerlendirilmiştir. Şekil 1 ve 2 UD kompozitlerin kırılma zarflarını göstermektedir. IPCBT kompozitin VE muadiliyle rekabet edebilir tasarım bölgesi koyu renkli olarak belirtilmiştir.

Kırılma zarflarına göre yapılan incelemelerde IPCBT kompozitlerinin özellikle tek yönlü baskı yüklemelerinde VE tabanlı kompozitlere güçlü bir alternatif olabileceği de anlaşılmıştır. Darbe dayanımının ise VE kompozitlerin dayanımından 2 katı daha fazla olduğu saptanmıştır.



Şekil 1 : IPCBT ve VE kompozitlerinin σ_2-σ_6 bölgesindeki kırılma zarfları



Şekil 2 : IPCBT ve VE kompozitlerinin σ_1-σ_2 bölgesindeki kırılma zarfları

Sonuç olarak, NCGF tekstili takviyeli IPCBT kompozitleri başırılı olarak üretilmiştir. Öncelikle IPCBT kompozitlerinde prepreg üretimi ve kompozit üretimi için en uygun proses değişkenleri belirlenmiştir. Literatür sonuçlarıyla kıyaslandığında prepgreglerden üretilen IPCBT kompozitlerinin RTM le üretilen ve bilinen PBT matrisli kompozitlere göre daha iyi eğme ve çekme özellikleri gösterdiği görülmüştür. RTM tekniği ve bilinen PBT kompozit üretim yöntemleriyle kıyaslandığında bu yeni yöntemle proses süresi ve enerji tüketiminin de düşürülebileceği gözlenmiştir. Ayrıca yapılan çalışmalarda, IPCBT kompozitlerinin prepreglerinden sadece baskıyla kalıplama yöntemiyle değil kompozitin çekme ve eğme dayanımında artış sağlayabilen vakumla kalıplama yötemiyle de üretilebileceği de görülmüştür.

PA matrisli NCGF takviyeli kompozitler de prepreglerden baskıyla kalıplama yöntemiyle başarıyla üretilmiştir. IPCBT kompozitlerinin çekme dayanımlarının PA kompozitlerinin çekme dayanımlardan daha yüksek olduğu tespit edilmiştir.

IPCBT ve PA prepregleri kullanılarak PA köpük ara malzemesi içeren sandviç yapılı kompozit plakalar da başarıyla üretilmiştir. Ancak yapılan ölçümlerde TP kompozit yüzeyi ile ara malzemenin arasındaki bağlanma mukavemetinin düşük olduğu saptanmış ve baskıyla kalıplamanın tek adımda sandviç plaka üretimine uygun olmadığı görüşüne varılmıştır.

1. INTRODUCTION

The polymers play very important role in our daily life. They can be combined with different materials to achieve special properties according to end use applications. Since the combinaton of them with the fibers improves their mechanical properties, fiber reinforced polymers are used in many applicaiton areas. In structural polimeric composite applications, textiles (e.g., unidirectional, woven fabrics) are commonly applied as reinforcement because of the high fiber volume fractions that can be obtained and because of the possibility to tailor the load bearing capacity through the fiber lay-up. Thermoset resins are used in textile reinforced composite industry as the matrix over 90% because of their easy process ability. Although, thermoplastic resins are used in niche market, mainly due to their difficulties in processing, they started to be an increasingly important issue in composite market [1-3]. The investigations on manufacturing of TP composites increased in recently years because of their advantages over thermoset composites such as ease of recycling, high toughness, impact resistance and the restrictions of health and environment rules [4-6]. Chopped fiber reinforced TP composites can be easily produced with extrusion and injection process but they are limited to non-structural applications because there is little control over fiber orientations due to the use of short fibers that flow with the matrix during processing and the relatively low fiber contents (i.e. less than 40% by weight). Continuous fiber reinforced TP composites have higher mechanical properties but they have limited production methods [7-11]. Traditionally, textile fiber-reinforced TP composites are processed by stacking alternating layers of fiber textiles and polymer sheets in a hot-press. After heating the package above the polymer melting point, the press is closed to obtain the required product shape. In a subsequent cooling step the product solidification takes place followed by demolding. Traditional melt processing, however, limits thermoplastic composite parts in size and thickness. The main problem in using thermoplastic resins is their high melt viscosity, which causes the poor impregnation of the fibrous reinforcement and the processing difficulties, necessitates higher pressures and adds expense [12]. In order to facilitate the fiber impregnation, reducing the required flow length of the polymer matrix by, e.g. using commingled yarns [13], or decreasing the viscosity during impregnation [14] are the main

methods investigated up today. One approach is the reactive processing of textile fiber-reinforced thermoplastics based on impregnation of the fibers with a low viscosity oligomeric precursor, followed by in situ polymerisation [15]. This approach has been studied recently with the using of cyclic oligomers, such as cyclic butylene terephthalate (CBT), have a low processing viscosity which can be called as water-like [16-18]. Because cyclic oligoesters can be transformed into linear high molecular weight thermoplastics with entropically driven ring-opening polymerisation in a short time, they can be processed under isothermal conditions. Therefore, the viscosity of the CBT matrix is sufficiently low and the processes which are currently associated to manufacturing of thermoset composites like resin transfer molding (RTM), vacuum infusion and resin film infusion, might be used for manufacturing of thermoplastic composite parts [19]. There are some records on reactive thermoplastic RTM, where the continuous reinforcement is impregnated with polymeric precursors following that a chemical reaction takes place to form thermoplastic matrix [15, 20]. Although RTM is useful process for production of continuous glass fiber reinforced composites, narrow impregnation time needed for complete wetting of the fibers, necessity of special equipment, time waste during resin mixing and infusion can be eliminate, the cost can be reduced by using pre-pregs [21-23]. Since the application of CBT for continuous fiber reinforced thermoplastic composites was concerned there is no a published work on the production of non-crimp glass fiber reinforced in situ polymerised CBT (IPCBT-NCGF) composites out of CBT coated prepregs.

1.1 Purpose of the Thesis

The current study focuses on the manufacturing of non-crimp glass fiber reinforced (NCGF) thermoplastic (TP) matrix composites. For this purpose, two kinds of TP resin were used as IPCBT and PA12 seperately. NCGF reinforced composite laminates were produced out of CBT/catalyst coated NCGF fabrics and PA12 coated NCGF fabrics via compression molding method. In this context, firstly pre-pregs (Prepreg is defined as a semi product composite material which is a fiber reinforcement impregnated with a resin) were manufactured by scattering of powder resin onto NCGF. All powder was fixed on fibers by heating and melting of the resin at its melting temperature. Afterwards, various composite laminates were produced with these prepregs by compression moldig in hot press. Several layers of pre-pregs were placed into a metal mold and compressed under pressure at a temperature higher then melting point of the resin. The effects of prepreg manufaturing

parameters such as temperature, time, production rate and the prepreg conditioning on end composites were investigated. Moreover, compression molding parameters such as temperature, time, pressure, and composite properties such as reinforcement type, fiber content and laminate thickness were investigated in order to determine most suitable composite production method considering the effects of them on mechanical properties and the processability of these pre-pregs. The analysis results of these composites were compared with those of composites produced by other methods in the literature.

1.2 Hypothesis

This study provided a new manufacturing method to produce thermoplastic composites including continuous glass fiber with various advantages such as time and energy saving, easy process ability, better composite properties when it is compared with other TP composites produced with different production methods. Moreover, newly initiated method provides recyclability, health and environment advantages when it is compared with its thermoset counter parts.

2. LITERATURE REVIEW

A composite, in general, is defined as a combination of two or more component differing in form or composition on a macro scale, with two or more distinct phases having recognizable interfaces between them [24]. Polymeric composites consist of a polymer as the matrix and reinfrocement which gives a specific property apart from matrix. The polymer matrix acts to hold the reinforcement material together and protect them, and to transfer the load to the reinforcement in the fabricated composite part. The reinforcing fibers, which are generally used in polymeric composites, impart strength and other required properties to the composite. Polymeric composites can be produced with two kinds of matrix polymer known as thermoplastic and thermoset. The common feature of thermoset polymeric composite processes is the combining of a resin, a curing agent (initiator), some type of reinforcing fiber, and in some cases a solvent. The curing agent, also known as hardener, acts as a catalyst and helps in curing the resin to a hard plastic. In the production of reinforced thermoplastic composites, heat and pressure are used to shape the mixture into a finished part. Reinforcement fibers can be found in several forms such as chopped, uni directional continuous, woven etc. The polymeric composites including chopped fiber can be produced by injection and extrusion of thermoplastic polymers. There are several methods to produce composites including continuous fiber reinforcement for both thermoset and thermoplastic matrices. These methods will be explained detailed in Section 2.4.

2.1 Continuous Fiber Reinforced Polymeric Composites (CFRPCs)

Fiber reinforced plastics are a subdivision of composites field in which the matrix is a polymer (or plastic) and the reinforcement is always a fiber. CFRPCs are typically organized in a laminate structure, such that each lamina (or flat layer) contains an arrangement of unidirectional fibres or woven fibre fabrics embedded within a thin layer of light polymer matrix material. The fibres, typically composed of carbon, glass or aramid, provide the strength and stiffness. The matrix, commonly made of thermosets such as polyester, vinylester, epoxy or thermoplastics such as PP, PA, PET, PBT binds and protects the fibers from damage, and transfers the stresses between fibers [25].

2.2 Reinforcement Materials Used in FRPCs

Fiber reinforcement materials are added to the resin system to provide strength to the finished part. The selection of reinforcement material is based on the properties desired in the finished product. These materials do not react with the resin but are an integral part of the advanced composite system.

2.2.1 Type of fibers

Three basic types of fiber reinforcement materials in use in the advanced composite industry are carbon, aramid, glass fibers.

2.2.1.1 Carbon fiber

The most commonly prefered reinforcement materials are carbon/graphite fibers. (The terms graphite and carbon are often used interchangeably.) This is due to the fact that many of the desired performance characteristics such as high tensile and compressive properties and high modulus values require the use of carbon/graphite fibers. Currently, these fibers are produced from three types of materials known as precursor fibers:

- polyacrylonitrile (PAN)
- rayon
- petroleum pitch

The carbon/graphite fibers are produced by the controlled burning off of the oxygen, nitrogen, and other noncarbon parts of the precursor fiber, leaving only carbon in the fiber. Following this burning off (or oxidizing) step, the fibers are run through a furnace to produce either carbon or graphite fibers. Carbon fibers are produced at furnace temperatures of 1,000-2,000°C, while graphite fibers require temperatures of 2,000-3,000° C. At these temperatures the carbon atoms in the fibers are rearranged to impart the required characteristics to the finished fiber. The PAN-based fiber is the more commonly used precursor in the advanced composite industry today. In the carbon fiber reinforced composites, the matrix polymer preferred is most often epoxy, but other polymers, such as polyester, vinyl ester or nylon, are sometimes used. The composite may contain other fibers, such as Kevlar, aluminium, or glass fibers, as well as carbon fiber. Although carbon fiber can be relatively expensive, it has many applications in aerospace and automotive fields, such as Formula One. The compound is also used in sailboats, modern bicycles and motorcycles, where its high strength-to-weight ratio and good rigidity is of importance.

2.2.1.2 Aramid fiber

Aramid fibers are another human-made product. These fibers are produced by manufacturing the basic polymer, then spinning it into either a paper-like configuration or into fiber. Aramid fibers have several useful characteristics such as high strength and modulus, temperature stability, flex performance, dimensional stability, chemical resistance, textile processability [26]. Aramid fibers have very low density and high specific tensile strength when compared to commonly available reinforcing fibers. They are best known for their use in bullet proof vests, chainsaw pants, safety gloves and other applications where cut resistance and damage tolerance are required. The main advantages of aramid fibers are [28]:

- Light weight
- High impact damage tolerance
- High tensile strength
- Moderately high tensile modulus (midway between E-glass & HS carbon)
- Excellent vibration damping
- Low (negative) longitudinal thermal expansion

The main disadvantages of aramid are:

- Very low compressive strength
- Susceptibility to UV radiation
- Difficult to machine
- High moisture absorption
- Very high transverse thermal expansion

2.2.1.3 Glass fiber

Glass fiber is an inorganic fiber which has an amorphous structure. It can be extruded into many fibers with small diameters suitable for textile processing. The technique consists of heating and drawing glass into fine fibers. By blending quarry products (sand, kaolin, limestone, colemanite) at 1600°C, liquid glass is formed. The liquid is passed through micro-fine bushings and simultaneously cooled to produce glass fibre filaments from 5-24m in diameter. The filaments are drawn together into a strand (closely associated) or roving (loosely associated), and coated with a coupling agent namely “sizing” to provide filament cohesion and protect the glass from abrasion. However, the choice and composition of ingredients varies to some extent depending on the end use requirements. There are different types of glass fibers commercially available all of which have different compositions and very often specific technical significance. AR-glass is alkali-resistant glass used in the form of fibers for reinforcement. C-glass has a chemically-resistant glass composition used for fiber manufacturing. E-glass has an almost universally acceptable formulation and has become a standard for most of the uses in fiber and relted products-the

letter ‘E’ stands for electrical, as the composition has a high electrical resistance. HS-glass is high strength glass fiber. Over 90% of all continuous glass fibers produced are ‘E’ glass composition [27, 28].

E Glass fibre is available in the following forms:

Strand - a compactly associated bundle of filaments. Strands are rarely seen commercially and are usually twisted together to give yarns.

Yarns - a closely associated bundle of twisted filaments or strands. Each filament diameter in a yarn is the same, and is usually between 4-13 micron. Yarns have varying weights described by their ‘tex’ (the weight in grammes of 1000 linear metres) or denier (the weight in lbs of 10,000 yards), with the typical tex range usually being between 5 and 400.

Rovings - a loosely associated bundle of untwisted filaments or strands. Each filament diameter in a roving is the same, and is usually between 13-24 micron. Rovings also have varying weights and the tex range is usually between 300 and 4800. Where filaments are gathered together directly after the melting process, the resultant fibre bundle is known as a direct roving. Several strands can also be brought together separately after manufacture of the glass, to give what is known as an assembled roving. Assembled rovings usually have smaller filament diameters than direct rovings, giving better wet-out and mechanical properties, but they can suffer from catenary problems (unequal strand tension), and are usually higher in cost because of the more involved manufacturing processes.

It is also possible to obtain long fibres of glass from short fibres by spinning them. These spun yarn fibres have higher surface areas and are more able to absorb resin, but they have lower structural properties than the equivalent continuously drawn fibres.

E-glass (“Electrical” grade glass) is by far the most used fiber in reinforced polymer composites. In many industries it represents over 90% of the reinforcements used. Its main advantages are:

- Low cost
- High strength
- Light weight (relative to steel)
- High chemical resistance

The main disadvantages are:

- Low modulus (relative to other reinforcing fibers)

- Low fatigue resistance (relative to carbon fibers)
- High weight (relative to other reinforcing fibers)
- Highly abrasive when machined
- Susceptibility to stress corrosion

Because of its widespread use, the advantages have a tendency to outweigh the disadvantages. Almost all glass fibers are sold in strands of grouped fibers, or rovings, associated with a particular yield. The yield is the number of yards of roving per pound. The metric unit of measure is TEX which is the weight in grams per kilometer (1,000 meters). The equation (2.1) for conversion between TEX and yield (YPP) is:

$$\text{Yield (yd/lb)} = \frac{496054.6}{\text{TEX}} \qquad \textbf{(2.1)}$$

$$\text{TEX (g/1,000m)} = \frac{496054.6}{\text{Yield}}$$

For stitch bonded reinforcement fabrics, typical roving sizes used range from 1800 to 113 yield (276 to 4390 TEX). Some common glass yields and filament diameters are given in Table 2.1 below:

Table 2.1 : Glass fiber yield points according to fiber diameter.

TEX (g/1000 m)	Yield (yield/lb)	Fiber diameter (µm)
44390	113	24
2400	206	17
1100	450	17
735	675	13
276	1800	13

The diameter of the individual filaments can be important because it represents the ratio of surface area of the fiber to its volume. Smaller filament diameters give higher surface area to volume ratios, which means there is more area for resin to bond to. Smaller filaments may give slightly better properties in some instances [27-28].

2.2.2 Surface treatment of the fibers: Compatibility between fiber and polymer

For adhesion to occur it is essential that intimate contact is established between the matrix and the fibre. The ability of the matrix to wet the fibre during processing depends on the relative surface tension between the fibre and the matrix. If the matrix surface tension is lower than that of the fibre, spontaneous wetting may occur as long as the viscosity of the matrix is favourable [5]. However, to ensure good interfacial adhesion and stress transfer across the interface, chemical or physical interactions between the matrix and the fibre need also to be formed. Coupling agents are used to provide a stable bond between two otherwise nonbonding and incompatible surfaces. They are molecules which have one end that is compatible the silane structure of the glass and the other end that is compatible with the matrix. They can be thought of as bridges connecting the reinforcement and the matrix [25]. In reinforced and filled plastics, the improved bond between the fibrous or particulate inorganic component and the organic matrix polymer results in greater composite strength and longer service life. Organofunctional silanes are the best known coupling agents for glass fiber, and their effect is based on their typical special chemical structure. $Y\text{-}Si(OR)_3$ is the main formula where OR is a hydrolyzable group such as methoxy, ethoxy, or acetoxy, and XY is an organofunctional group such as amino, methacryloxy, epoxy, etc. These two type of groups exhibit different reactivity and allow sequential reactions. In the crosslinking process, the first step is generally the grafting of the silane the polymer backbone the linking of the polymer chains via condensation of silanols. An amino or chloropropyl functional silane on the surface of the glass lends itself to coordination with the amidegroups and possibly coupling of polyamides to the glass surface. For aramid fibers non-ionic emulsifiers containing ethylene oxide and propylene oxide tails are the most common process aids during fiber spining process as a coupling agent [30].

2.2.3 Forms of reinforcements

Fibers used in advanced composite manufacture come in various forms, including yarns, rovings, chopped strands, woven fabric, mats. Each of these has its own special application. When prepreg materials are used in parts manufacture, woven fabric or mats are required. In processes such as filament wet winding or pultrusion, yarns and rovings are used [26]. Table 2.2 demonstrates different reinforcement forms and their application areas with the advantages [24].

Table 2.2 : Reinforcement forms and application areas with advantages.

Reinforcement	**Advantages**	**Applications**
Tape	High stregth and stiffness in one direction	Sports goods Aircraft primary structures
Single Tow	Suitabe for filament winding Very narrow width for accurate fiber placement (1mm)	Prsessure vessels Drive shafts Tubes
Strips	High strength and stiffness in one direction High fiber weights=1000g/m2 Economic processing	Yact masts Leaf springs Skis
Fabrics>80% warp	For composnents requiring predominant strangth and stiffness in one direction Weights from 160-1000g/m2	Aerospace Insutrial Sport leisure
Balanced fabrics	Strength and stiffness in two directions Very good handling characteristics Good drape Choice of weave styles Possible to mix fibers Weight from 20 to 1000 g/m2	Aerospace Industrial Sport and lesiure
Multiaxials	Strangth and stiffness in multiple drections Control of fber orientation Abilitiy to optimise weight distibution in fabric Possible to mix fibers No crimp Less waste for complex lay-ups Reduced processing cost Heavy weights achievable	Aeropspace Marine Pipe Automotive Wind tribuns Sports and lesiure Indusrial

Continuous filament reinforcements are very important materials for high-end applications such as aerospace; the orientation of the fibrous reinforcement is becoming more and more important from a load-bearing point of view as well as the need for placing the reinforcement oriented in the third dimension. In this context, the use of textile structures made from high-performance fibers is finding increasing importance in composites applications. In textile processes, there is direct control over fiber placements and ease of handling of fibers. In addition to economic advantages, textile technologies also provide homogenous distribution of matrix and reinforcing fiber. Thus, textile preforms are considered to be the structural backbone of composite structures [15].

Woven and non-crimp multiaxial reinforcements are most commonly used reinforcement forms in composite structures. Multiaxial (non-crimp) reinforcements provide many advantages over woven fabrics such as:

• Increased mechanical properties of end-product
• Reduced weight of end-product
• Design flexibility
• Lower resin consumption
• Faster and easier wet-out
• Improved surface quality; reduction of print-through effect;
• Reduced lay-up time
• Reduced labor costs
• Increased output

Figure 2.1 illustrates these advantages with a basic comparison of a woven fabric and a non-crimp 0°/90° reinforcement. Resin pocket and crimp effect cause higher resin consumption, low mechanical properties and cracking. Besides, non-crimp structure reduces the resin consumption and increases mechanical properties [29].

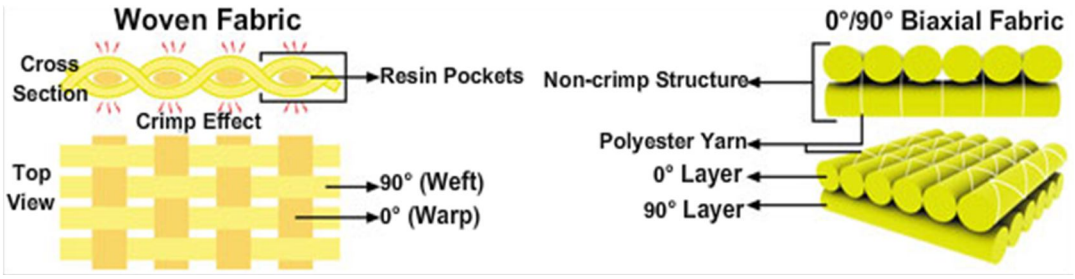


Figure 2.1 : Differences between woven and multiaxial reinforcements [29].

Woven fabrics can be found in different forms according to their weaving types, See Fig. 2.2.

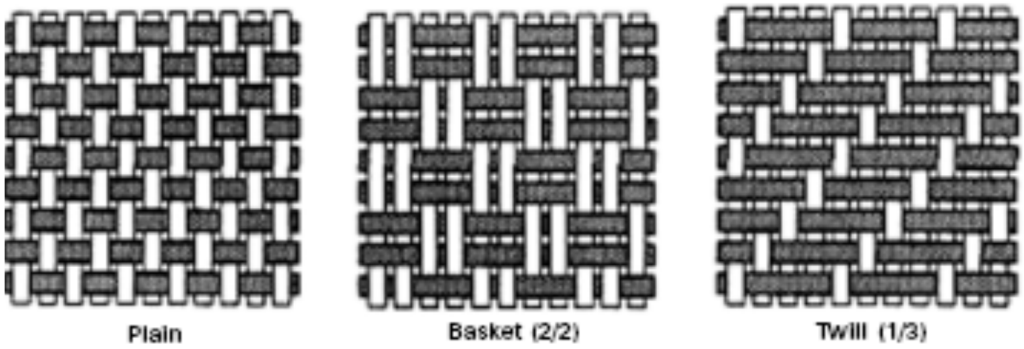


Figure 2.2 : Woven fabrics from high tenacity fibers [29].

Multiaxial reinforcements can consist from four layers where fiber orientations are in all basic directions; 0/+45°/90/-45°. Fibers are generally stabilised by stitching using flexible thermoplastic yarns (PET, PBT, PA etc.) to avoid any possible damage during handling and processing of the reinforcement. Stitching pattern can vary as

being stiff or flexible according to requirements of composite production process. Figure 2.3 represents a basic scheme of a multiaxial reinforcement which includes all possible directions and the other elements.

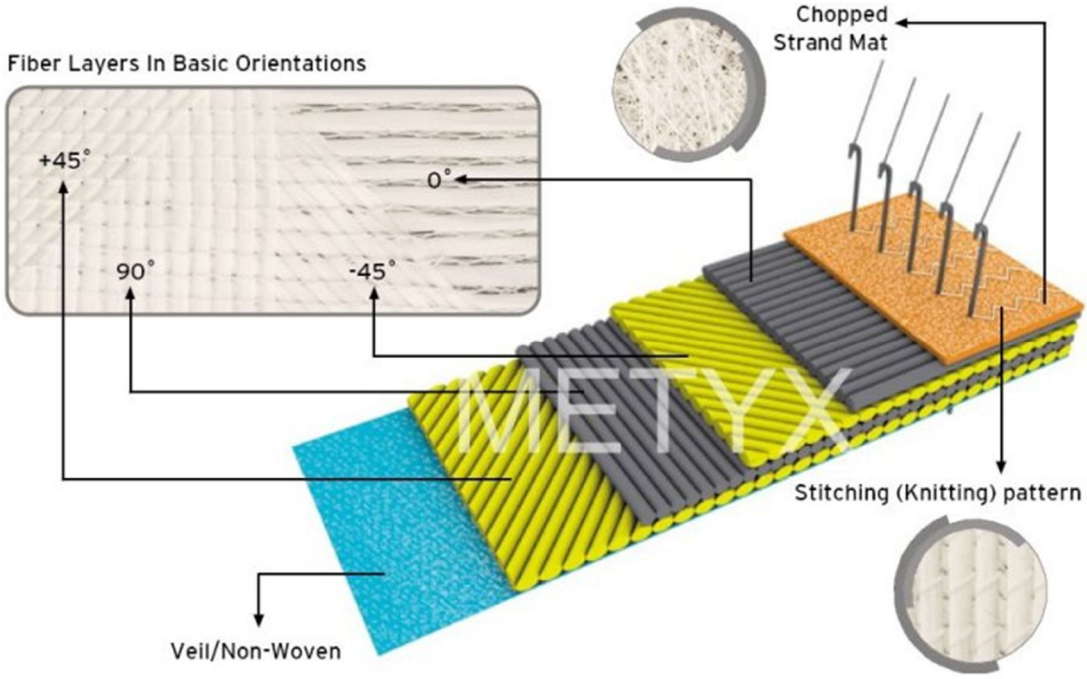


Figure 2.3 : Basic scheme of a multiaxial structure [29].

Non crimp multiaxials can consist of fiber layers varying form uniaxial to quadriaxial. Non crimp multiaxials including different numbers of layers can be seen in Figure 2.4.

Figure 2.4 : Non crimp multiaxials including different numbers of layers [29].

2.3 Polymer Systems in CFRPCs Production

The polymer systems used to manufacture advanced composites are of two basic types: thermosetting and thermoplastic. Thermosetting polymers predominate today, while thermoplastics have only a minor role in advanced composites manufacture [26]. Polymer matrix material is called as the resin in composite industry.

2.3.1 Thermoset polymers

Thermosetting materials, or 'thermosets', are formed from a chemical reaction in situ, where the polymer and hardener or resin and catalyst are mixed and then undergo a non-reversible chemical reaction to form a hard, infusible product. Thermoset resins require addition of a curing agent or hardener and impregnation onto a reinforcing material, followed by a curing step to produce a cured or finished part. Once cured, the part cannot be changed or reformed, except for finishing. Although there are many different types of resin in use in the composite industry, the majorities of structural parts are made with three main types, namely polyester, vinylester and epoxy.

Polyester resins are the most widely used resin systems, particularly in the marine industry. Polyester resins such as these are of the 'unsaturated' type. Unsaturated polyester resin is a thermoset, capable of being cured from a liquid or solid state when subject to the right conditions. Most polyester resins are viscous, pale coloured liquids consisting of a solution of polyester in a monomer which is usually styrene. The addition of styrene in amounts of up to 50% helps to make the resin easier to handle by reducing its viscosity. The styrene also performs the vital function of enabling the resin to cure from a liquid to a solid by 'cross-linking' the molecular chains of the polyester, without the evolution of any by-products. These resins can therefore be molded without the use of pressure and are called 'contact' or 'low pressure' resins. Polyester resins have a limited storage life as they will set or 'gel' on their own over a long period of time. Often small quantities of inhibitor are added during the resin manufacture to slow this gelling action. For use in molding, a polyester resin requires the addition of several ancillary products. These products are generally: Catalyst, accelerator, additives [26, 28].

Vinylester resins are similar in their molecular structure to polyesters, but differ primarily in the location of their reactive sites, these being positioned only at the ends of the molecular chains. With the reduced number of ester groups in a vinylester when compared to a polyester, the resin is less prone to damage by hydrolysis. The material is therefore sometimes used as a barrier or 'skin' coat for a polyester laminate that is to be immersed in water, such as in a boat hull. The cured molecular structure of the vinylester also means that it tends to be tougher than polyester, although to really achieve these properties the resin usually needs to have an elevated temperature postcure [28].

Epoxy resins have been in use in the industry for over 40 years. The basic epoxy compounds most commonly used in industry are the reaction product of epichlorohydrin and bisphenol-A. Epoxies differ from polyester resins in that they are cured by a 'hardener' rather than a catalyst. The hardener, often an amine, is used to cure the epoxy by an 'addition reaction' where both materials take place in the chemical reaction. The chemistry of this reaction means that there are usually two epoxy sites binding to each amine site. This forms a complex three-dimensional molecular structure. Usually identifiable by their characteristic amber or brown colouring, epoxy resins have a number of useful properties. Both the liquid resin and the curing agents form low viscosity easily processed systems. Epoxy resins are easily and quickly cured at any temperature from 5°C to 150°C, depending on the choice of curing agent. One of the most advantageous properties of epoxies is their low shrinkage during cure which minimizes fabric 'print-through' and internal stresses. High adhesive strength and high mechanical properties are also enhanced by high electrical insulation and good chemical resistance.

The second of the essential ingredients of an advanced composite system is the curing agent or hardener. These compounds are very important because they control the reaction rate and determine the performance characteristics of the finished part. Since these compounds act as catalysts for the reaction, they must contain active sites on their molecules [24].

2.3.2 Thermoplastic polymers

Thermoplastics currently represent a relatively small part of the PMC industry. They are typically supplied as nonreactive solids (no chemical reaction occurs during processing) and require only heat and pressure to form the finished part. Unlike the thermosets, the thermoplastics can usually be reheated and reformed into another shape, if desired.

Thermoplastic polymers can be divided into two classes, high temperature thermoplastics and the engineering thermoplastics. The classification is based on the maximum service temperature of the polymers, which in turn is based on the Glass Transition (Tg) temperature. Thermoset polymers may not usefully carry mechanic loads above Tg, but semi-crystalline thermoplastic polymers may carry load above Tg, as only the amorphous phase of the polymer has become rubbery. The crystalline portion of the polymer remains solid until the melt temperature, Tm. [31].

Table 2.3 shows the most commonly used high temperature thermoplastic polymers for thermoplastic composites. Table 2.4 shows the engineering thermoplastic polymers used in composites.

Table 2.3 : High temperature thermoplastics.

Matrix	Morphology	Tg (°C)	Process Temp (°C)	Cost (Relative)
PEEK	SC	143	390	$$$
PEI	A	217	330	$$
PPS	SC	89	325	$
PEKK	SC	156	340	$$

Table 2.4 : Engineering thermoplastics.

Matrix	Morphology	Tg (°C)	Process Temp (°C)	Cost (Relative)
PBT	SC	56	190	$$
PA-6	SC	48	220	$
PA-12	SC	52	190	$
PP	SC	-20	190	$

The vast number of thermoplastic resins used in composite materials can conveniently be separated into two categories:

1. The traditional industrial (engineering) thermoplastics which have been used with short fiber reinforcements for many years.

2. A new set of high-performance thermoplastics which have been developed specifically for use in advanced composites.

The conventional or industrial plastics which are common in our everyday lives (polyethylene, nylon, polystyrene, polyester, polycarbonate, acrylic etc.) can also be reinforced to improve their strength and rigidity. The choice of which conventional resin to use is often dictated by properties associated with the resin, such as cost, environmental resistance, processability, lubricity, resistance to creep, or many others [25].

2.3.3 Advantages and disadvantages of thermoplastic & thermoset matrices

The inherent differences between thermoplastics and thermosets give each type of resin some distinct advantages over the other. Thermoplastics do not require reactive cure cycles, but are supplied as essentially nonreactive solids which require only heat and pressure with subsequent cooling to form them. This has obvious savings in processing time and equipment costs, but for some processes requires that the resin diffuse quickly to coat the reinforcement during the relatively short period of time that the resin has low viscosity. On the other hand, cured thermosets have much higher molecular weights (since all the polymer chains are tied into one large network), and this results in improved strength and modulus, but diminished elongation and toughness. Furthermore, fibrous sheets already impregnated with resin (prepregs) which are made from thermoplastics have an infinite shelf life, compared to the limited life of thermoset prepregs. The thermoplastic prepregs are stiff and without drape or tack which are present in the thermosets before curing. It is obvious, therefore, that in the choice of thermoplastic versus thermoset resin, several tradeoffs and compromises must be made. A summary of these trade-offs is given in Table 2.5 [25].

Table 2.5 : Comparison of typical thermoset versus thermoplastic.

	THERMOSET (FIBERITE 931 EPOXV)	THERMOPLASTIC (ICI APC-2 PEEK)
Melt Viscosity	Low	High
Fiber İmpregnation	Easy	Difficult
Prepreg Tack	Good	None
Prepreg drape	Good	Poor
Prepreg Stability at 0F	6 mos.-1 yr.	Indefinite
Processing Cycle	1-6 hrs.	15 Sec.-6 hrs.
Processing Temperature	350°F	700°F
Mechanical Properties	Good	Good
Environmental Durability	Good	Exceptional
Damage Tolerance	Average	Good
Database	Large	Average

The single biggest advantage of thermoset polymers is that they have a very low viscosity and can thus be introduced into fibres at low pressures. Impregnation of the fibres is followed by chemical curing to give a solid structure, which can usually be carried out isothermally. An advantage of thermoplastics is that the molding can be carried out non-isothermally, i.e. a hot melt into a cold mold, in order to achieve fast cycle times. However, polymerised thermoplastics tend to have melt viscosities between 500 and 1000 times that of thermosets, which necessitates higher pressures, causes processing difficulties and adds expense.

Thermoplastic composite polymers can, however, be readily recycled, an increasingly important issue in many markets, but especially in the automotive sector. For instance, an advanced thermoplastic composite component can be chopped to pellet-size and injection-molded to yield long-fibre reinforced moldings, which can in turn be recycled at the end of their life. Thermoset composite materials, on the other hand, can only be ground and used as filler, a process which decreases the value of the composite enormously.

Another advantage of thermoplastic composites are their superior impact and damage resistance properties. Over 90% of polymers used in composites are thermosets, with thermoplastic composites still a niche market, mainly due to the difficulties in processing.

There are also significant environmental issues associated with thermoset processing, as a chemical reaction is necessary to form the solid structure of the polymer. Approximately 65% of thermoset matrices used in structural composites are unsaturated polyesters. Environmental regulations regarding the styrene emissions of unsaturated polyester are affecting the total cost associated with using them. Because of this, many people are willing to consider a substitute for unsaturated polyester at a higher price.

In summary, thermoplastic composites to date have needed high processing pressures, and hence expensive product tooling, as well as significant energy input in heating and cooling the tooling. These disadvantages have in many areas outweighed the advantages of these materials such as ease of recycling and high toughness, and limited their applications. On the other hand, thermoset composites are easier to process, requiring less energy and pressure, but are inherently brittle and cannot be usefully recycled [25, 31].

2.4. CFRPCs Manufacturing Methods

2.4.1. Manufacturing with thermoset resins

2.4.1.1 Prepregging

Prepregging involves the application of formulated resin products, in solution or molten form, to reinforcement such as carbon, fiberglass or aramid fiber or cloth. The reinforcement is saturated by dipping through the liquid resin (Figure 2.5). In an alternate method called a hot melt process the resin is impregnated through heat and pressure. The hot melt system uses resins with a very low percentage of solvents.

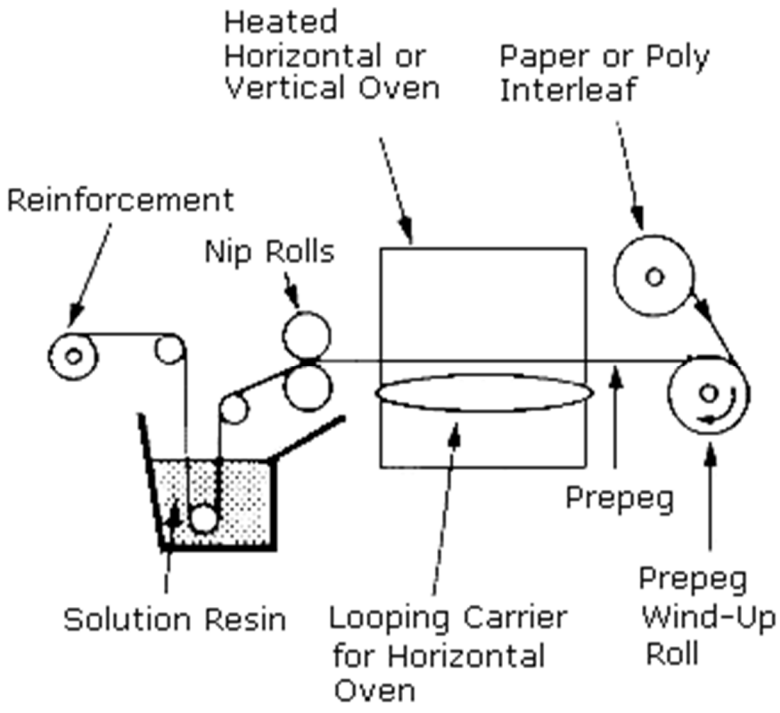


Figure 2.5 : Representation of prepreg production method [26].

2.4.1.2 Wet filament winding

In the filament wet winding process, continuous fiber reinforcement materials are drawn through a container of resin mixture and formed onto a rotating mandrel to achieve the desired shape (Figure 2.6.). After winding, the part is cured in an oven. This process can also used preimpregnated fiber tows called towpregs.

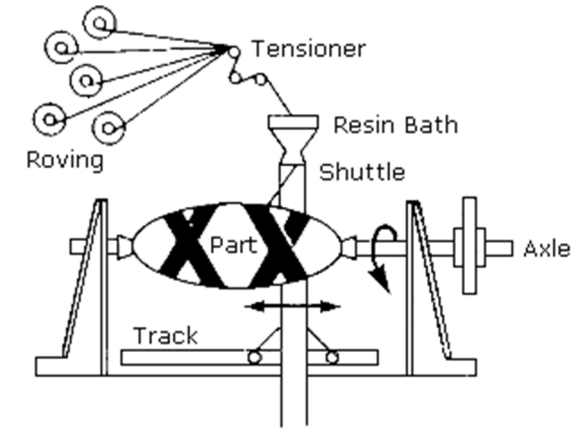


Figure 2.6 : Representation of filament winding method [26].

2.4.1.3 Hand lay-up of prepreg

The prepreg product is trimmed and laid down over a mold where it is formed to the desired shape. Several layers may be required. After forming, a vacuum bag is sealed around the lay-up (2.7). Vacuum is pulled on the raw prepreg to remove air, compact the part and serve as a barrier when the assembly is placed in an autoclave for cure under heat and pressure. Oven cures (under vacuum only) may be used for non-structural parts.

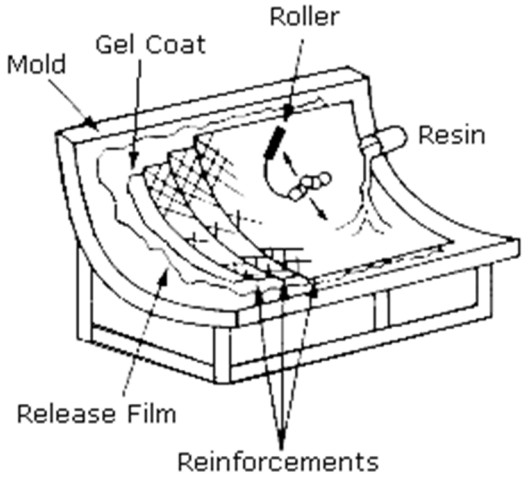


Figure 2.7 : Representation of hand lay-up method of prepreg [26].

2.4.1.4 Resin transfer molding (RTM)

RTM is used when parts with two smooth surfaces are required or when a low-pressure molding process is advantageous. Fiber reinforcement fabric or mat is laid by hand into a mold and resin mixture is poured or injected into the mold cavity (Figure 2.8). The part is then cured under heat and pressure.

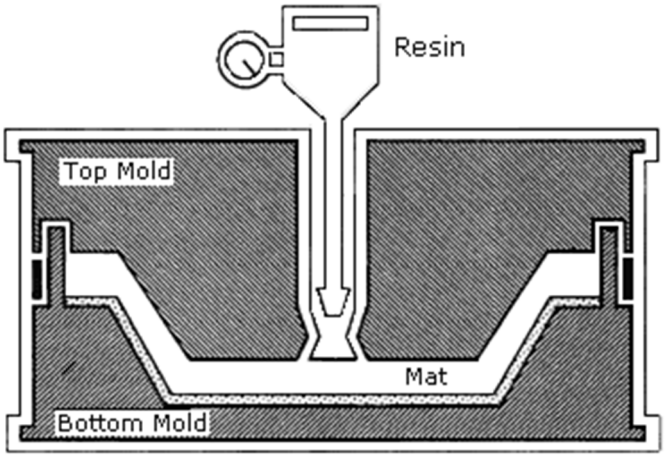


Figure 2.8 : Representation of RTM [26].

2.4.1.5 Infusion process

Fabrics are laid up as a dry stack of materials as in RTM. The fibre stack is then covered with a peel ply fabric and a knitted type of non-structural fabric. The whole dry stack is then vacuum bagged, and once bag leaks have been eliminated, resin is allowed to flow into the laminate. The resin distribution over the whole laminate is aided by resin flowing easily through the non-structural fabric, and wetting the fabric out from above (Figure 2.9.) Fibres: Any conventional fabrics. Stitched materials work well in this process since the gaps allow rapid resin transport [32].

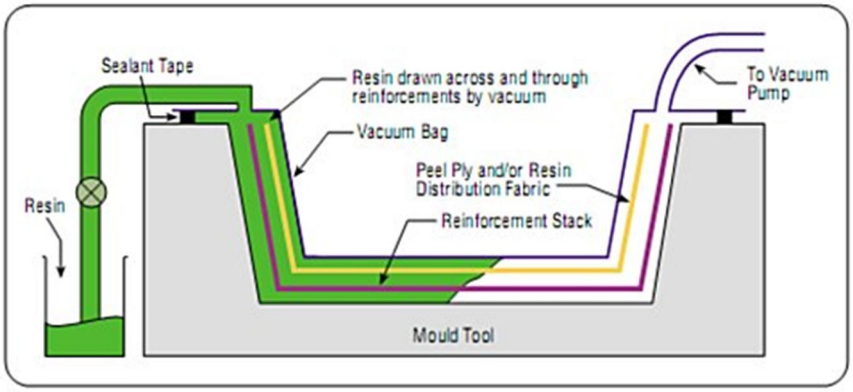


Figure 2.9 : Representation of infusion process [29].

2.4.1.6 Vacuum bagging, autoclave cure

Most parts made by hand lay-up or automated tape lay-up must be cured by a combination of heat, pressure, vacuum, and inert atmosphere. To achieve proper cure, the part is placed into a plastic bag inside an autoclave (Figure 2.10). A vacuum is applied to the bag to remove air and volatile products. Heat and pressure are applied for curing. Usually an inert atmosphere is provided inside the autoclave

through the introduction of nitrogen or carbon dioxide. Exotherms may occur if the curing step is not done properly.

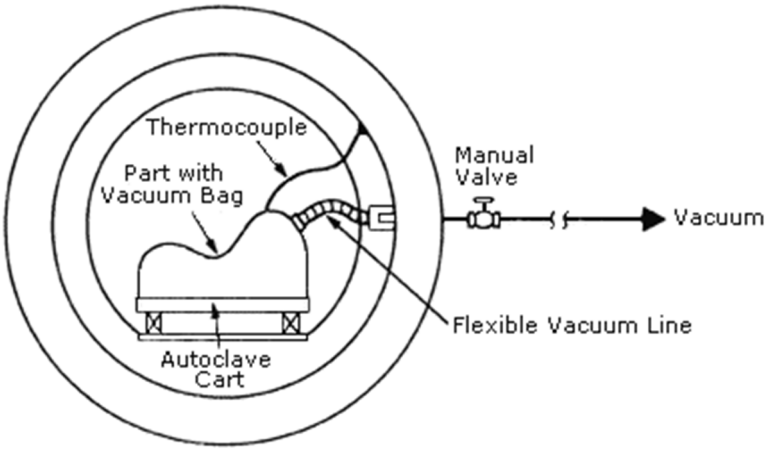


Figure 2.10 : Representation of vacuum bagging in autoclave [26].

2.4.2 Manufacturing with thermoplastic resins

The short fiber reinforced thermoplastics are more commonly used in composite manufacturing because using discontinuous (or chopped, short etc.) fibers shows less problems. The mixing fibers and matrix in an extruder or injection can solve the processing problems due to the high melt viscosity of the matrix by introducing high shear forces that allow the fibers to be distributed evenly into the matrix. However, in structural composite applications short fiber reinforced thermoplastics do not meet the needs of applications. Therefore, textiles are commonly applied as reinforcement because of the high fiber volume fractions that can be obtained and because of the possibility to tailor the load bearing capacity through the fiber lay-up.

There are important two stages which have to done to achieve of well wetted CFRPC with TP matrix. First stage is to provide intimate mechanical mingling of the fiber and the matrix. Second stage is impregnation and consolidation using a combination of heat and pressure. The first stage is critical as it brings together the resin and reinforcement in such away that it minimises the subsequent flow length required to achieve impregnation and creats the reinforcing synergy in the final structure. Figure 2.11 represents impregnation of fibre bundle by resin under pressure.

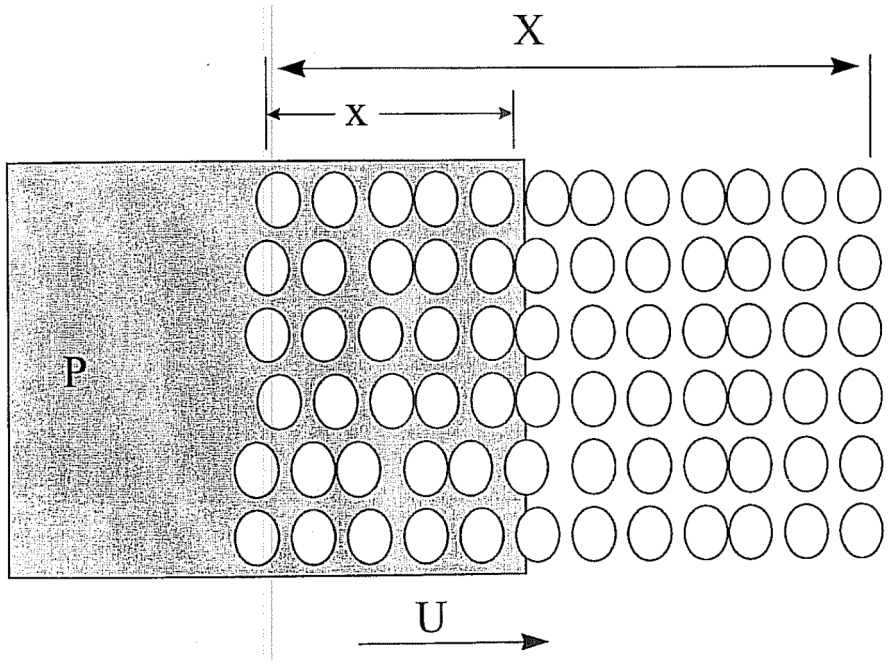


Figure 2.11 : Impregnation of a fiber bundle by resin under an applied pressure[21].

A flow length, X, can be used to describe the distance that the resin must flow to achieve the required impregnation level at the end of stage 1. For stage 2 a simple model relates the flow velocity (U) of the resin in the fiber bundle from Equation 2.2. where S is the permability of the fiber bundle, η is the matrix viscosity and P is to applied pressure.

$$U = \frac{dx}{dt} = \frac{SP}{\eta x} \tag{2.2}$$

By integrating this equation and assumng a constant permeability during the impregnation process, the time required to fully impregnate fibers bundle, t_{imp} can be estimated by Equatin 2.3.,

$$t_{imp} = \frac{\eta X^2}{2SP} \tag{2.3}$$

Equation 2.3 demonstrates the main parameters that influence the impregnation process. The obvious objective when processing composites is to minimise the impregnation time and it is demonstrated from equation that this can be achieved by minmising the required flow length, X. As the viscosity of thermoplastic resins is much higher than those of thermosets, it follows from the equation that thermoplastic systems can not be processed using the same techniques. The

impregnation process can be accelerated by increasing the applied pressure, but the maximum that can be applied is limited by the compression resistance of the fibers. It can be seen that particular processing techniques need to be aplied to manufacture these high viscosity resin composites at intermadiate pressure. A number of different techniques have been developed, yet they can be grouped into two principal areas; a process which aims to reduce the viscosity in orde to achieve rapid impregnation, the pre-impregnation process, and the process that aims to reduce the distance that the resin is required to flow which involve intimate mixing of constitutents prior to melting, the mingling process. Figure 2.12 shows alternative process routes of CFRPCs with TP matrix.

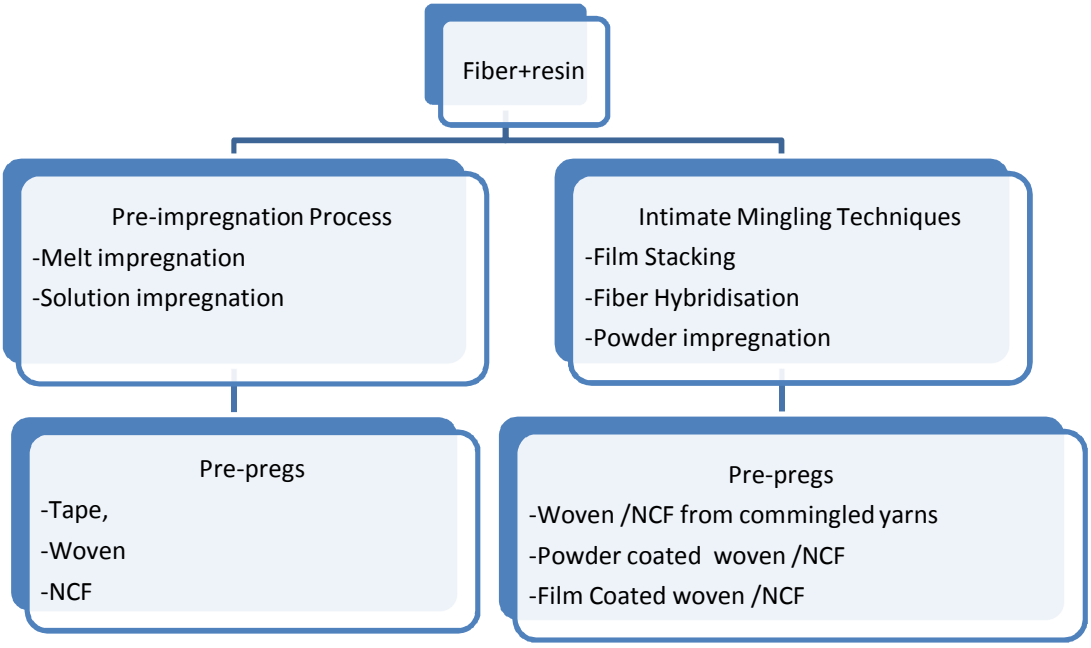


Figure 2.12 : Alternative processing routes for CFRTPCs [21].

2.4.2.1 Film stacking

Film stacking of textiles is melt processed by stacking alternating layers of fiber textiles and polymer sheets in a hot-press. After heating the package above the polymer melting point, the press is closed to obtain the required product shape. In a subsequent cooling step the product solidification takes place followed by demolding. Although this process is simple and less expensive than the others, it has disadvantages.It is difficult to achieve complex shapes because the stacks are not very drapeable. Moreover, the mingling intimacy is rather low and therefore this technique is not suited for very dense fabrics and high fiber volume fractions [21].

2.4.2.2. Hybrid yarns and fabrics

Hybridisation of thermoplastic fibers and reinforcing fibers is another method for intimate mingling techniques. A hybrid yarn consists of a blended combination of reinforcing filament yarn and filament yarn spun from thermoplastic polymers. The multifilament yarns are distributed amongst one another at filament level. Hybrid yarns can be manufactured by various means, including co-wrapping, core spinning and commingling, aiming to give uniform distribution of matrix and reinforcement fibers as well as to reduce the damage to reinforcing fibers.

In co-wrapping, thermoplastic fibers are wrapped around a core of reinforcing fibers. This provides better protection for the reinforcing fibers during further processing, such as weaving or braiding. However, inhomogeneous distribution of the reinforcing and matrix yarns may lead to poor impregnation and does require higher processing temperatures and pressures. In friction spinning or core spinning, short thermoplastic fibers are spun around a core of continuous reinforcing fibers.
In commingling, the reinforcing and matrix fibers are intimately mixed in a nozzle by means of compressed air. Among these hybrid yarns, commingled yarns provide high potential for thorough blending of matrix-forming filaments and high-performance fibers [9, 11].

Another commingling method namely “online commingling” was developed to avoid fiber damage during air pressure application. In this method commingling is made by separate spinning of E-glass fibre (GF) and TP filaments [10]. After preforming of hybrid yarns into the woven or NCF, hybrid preforms can be consolidated to form an end composite by compression or vacuum consolidation [13, 33]. Figure 2.13 demonstrates various hybrid yarn types produced with different hybridisation methods [9].

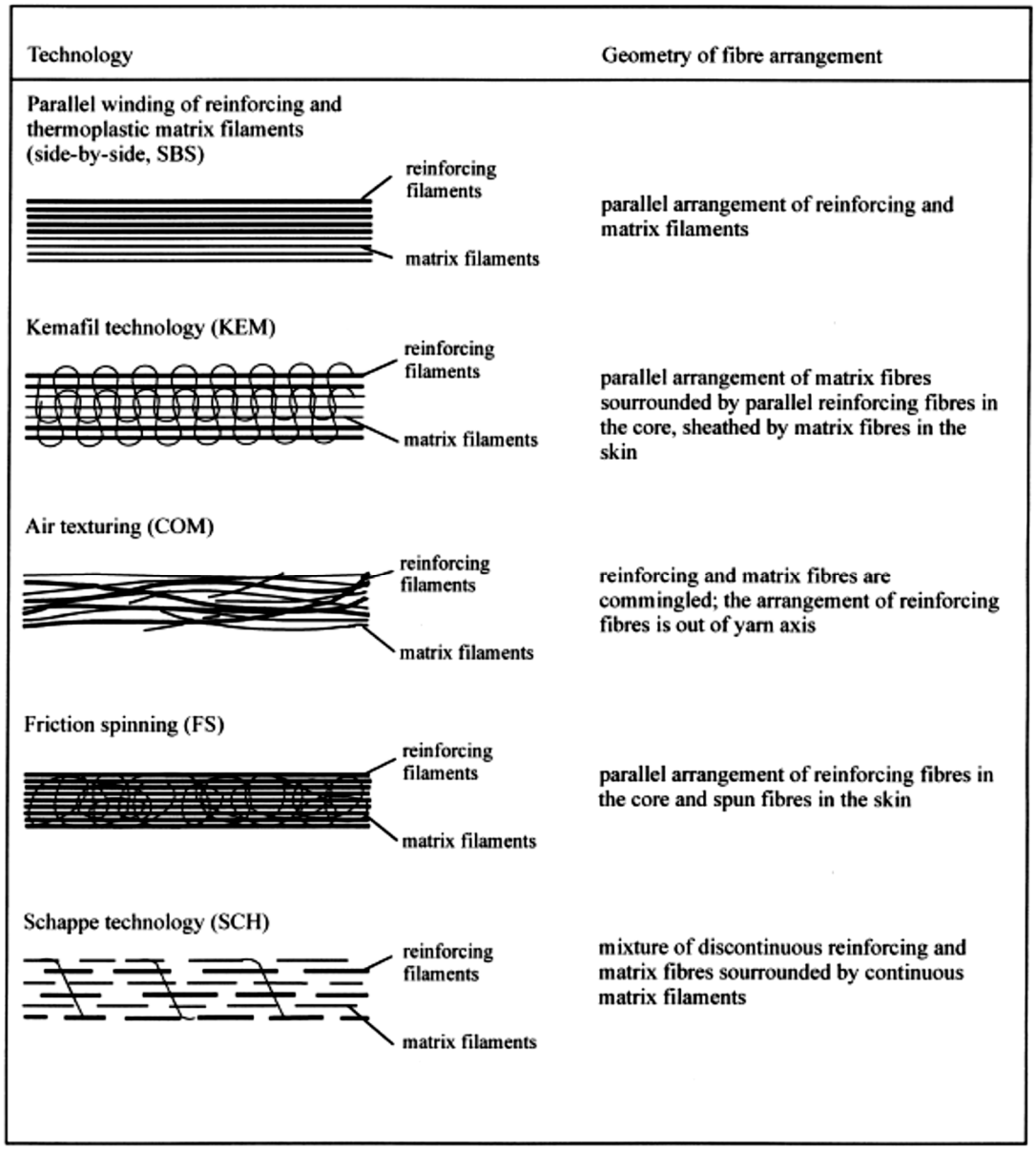


Figure 2.13 : Hybrid yarn structures and corresponding production technology [9].

2.4.2.3 Powder impregnation

In powder impregnation technique, thermoplastic powder particules were incorporated into the fibres. The dry powder particles adhere electrostatically to the fibres but since these forces are too weak, to stabilise the powder to the fibre surface the system is subsequently heated by passing it through an oven. The advantages of dry powder porcess over other processes can be summiresed as follows [21, 34]. The reduction in flow length required for impregnation which takes place paralel, rather than perpendicular to the fibres, allows for processing of low and high viscosity matrices.

- The process can be used with any matrix which can be provided in powder form, and at a much lower cost than fiber spinning
- There is no need to evaporate any binder, water or solvent before forming
- The process is relatively simple
- Highy flexible preforms can be obtaned allow the formation of complex parts

Powder impregnated preforms can be shaped using various techniques such as rubber diaphgram forming, rubber stamping, compression by heating, vacuum bagging in autoclave and filament winding [21, 35].

2.4.2.4 Melt impregnation

In the case of melt impregnation the fibre bundle is spread to aid melt penetration prior to entering a crosshead extruder and die which is normally designed to produce a thin flat tape or prepreg. The process, which is shown in figure 2.14, is capable of offering desired tape widths and thicknesses [36].

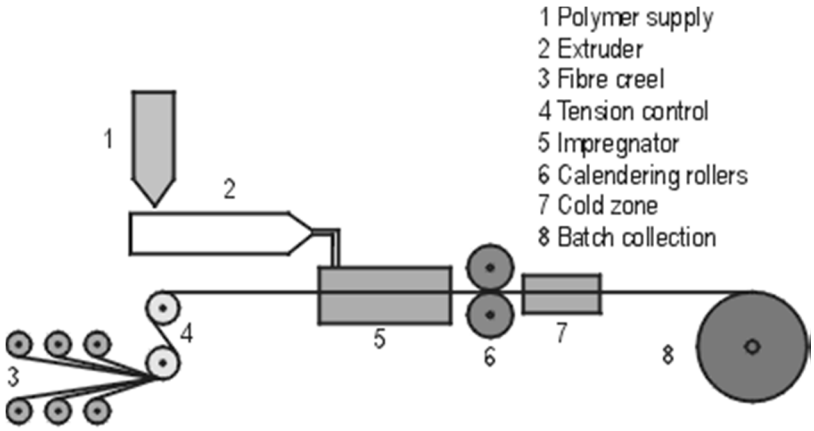


Figure 2.14 : Representation of a melt impregntaion process [36].

2.4.2.5 Solvent impregnation

In this method polymer has to be dissolved in a solvent to reduce viscosity. Solvent impregnation requires the polymer to be dissolved in a solvent to reduce the viscosity during impregnation. After wet-out of the fibers was completed, the solvent must be removed. This removing can result void formation during evaporation. Moreover, complete removel of solvent is very difficult compromising further processing and reduces service performance [21].

2.4.2.6 Reactive processing of thermoplastics

Reactive processing of thermoplastics was developed as an alternative solution to other methods mentioned above in recently years. In this process after impregnating the fibers with a low viscosity precursor (monomer or oligomer), polymerisation of the thermoplastic matrix is conducted in situ. Polymerisation can be initiated by heat and requires the addition of a catalyst system, which can be added to the precursor prior to impregnation. Due to their low molecular weight, precursors have extremely low melt viscosities and proper fiber impregnation is therefore achieved without the need for high processing pressures. Moreover, through reactive processing, textile fiber reinforced TP composites can be even manufactured through lowpressure infusion processes such as RTM and vacuum infusion [15].

Reactive thermoplastic materials

For reactive processing of thermoplastic composites, in situ polymerisation of the matrix basically has to meet the following requirements: a high molecular weight linear polymer has to be formed at sufficiently high conversions without the generation of unwanted by-products. Suitable polymerisation types are consequently narrowed down to addition polymerisations of mono- and difunctional species, of which vinyl polymerisation and ring-opening polymerisation are most common.

Caprolactam and laurolactam can be anionically copolymerised to tailor polymer properties. Polyamide-12 is anionically polymerised from ω-laurolactam (Tm=154 ºC) with activators and initiators. When processing at 180–240 ºC, an additional cooling step is required prior to demolding. The molten monomer has an initial viscosity of 23 mPa s. Anionic ROP of e-caprolactam (Tm = 69 ºC) into high molecular weight polyamide-6 (PA-6), see Fig. 2.15, is a catalyzed reaction performed at 130–170 ºC. Final conversions of up to 99.3% can be obtained in 3–60 min., depending on the type and amount of activator and catalyst added. The process difficulites of polyamides is that precursor/catalyst mixing has to be kept in nitrogen protective environment to prevent initiator deactivation [15, 37, 38].

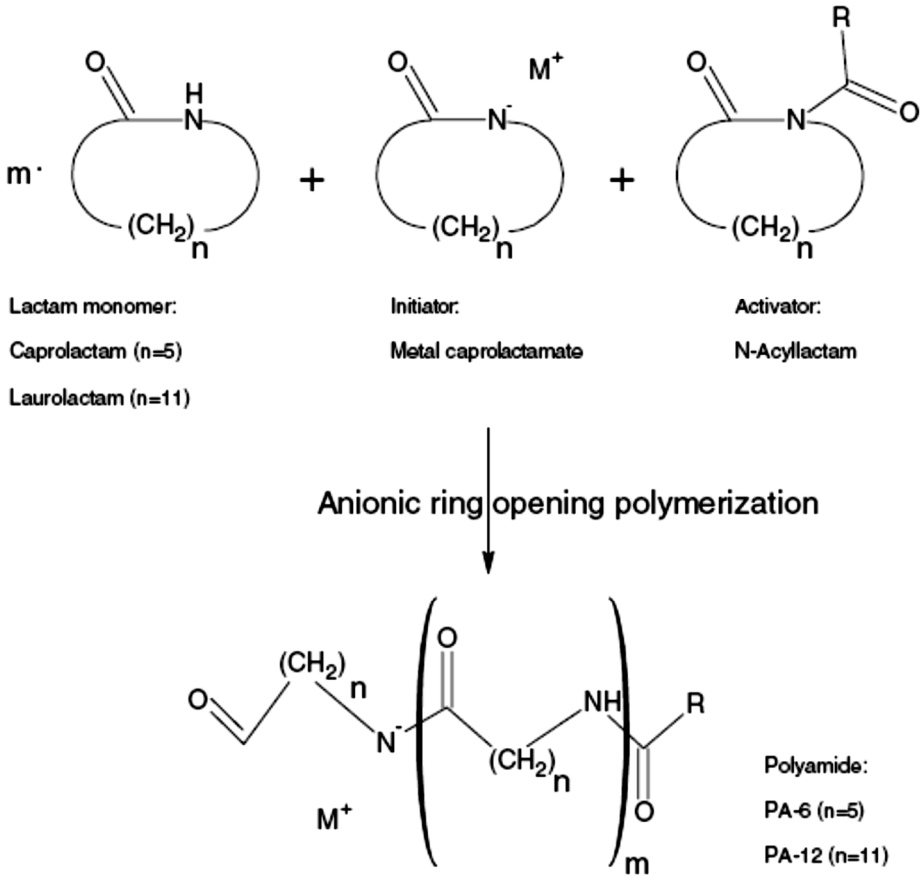


Figure 2.15 : Anionic ring-opening polymerisation of polyamides [15].

Synthesis of macrocyclic polyesters and the ring-opening metathesis polymerisation (ROMP) there of was initially developed by D.J. Brunelle and his research group at the General Electrics Corporation, USA, in the late 1980s and early 1990s. Macrocyclic oligomers can be obtained through cyclodepolymerisation (CDP) of linear PET and subsequently repolymerised through ROMP into high molecular weight PET. Up to 100% conversion at 250–325 ºC are obtained in several hours without a catalyst, whereas addition of a catalyst reduces the reaction time to 3–15 min at 225 ºC. The initial melt viscosity of the cyclic precursors is 30 mPa s [39, 40]. Depolymerisation of linear PBT yields a macrocyclic oligomer mixture namely CBT, which can be repolymerised directly into solid high molecular weight (Mw = 445,000) semi-crystalline PBT at 180–200 °C by addition of a titanium initiator [41]. CBT resins are available in two forms as with and without polymerisation catalyst. CBT will be explianed in section 2.6 detailed.

There are various thermoplastic researched which can be polymerised from their precursors. Figure 2.16 summurizes thermoplastics plastics with their melt viscosity and process temperatures comparing with thermosets and each other [15].

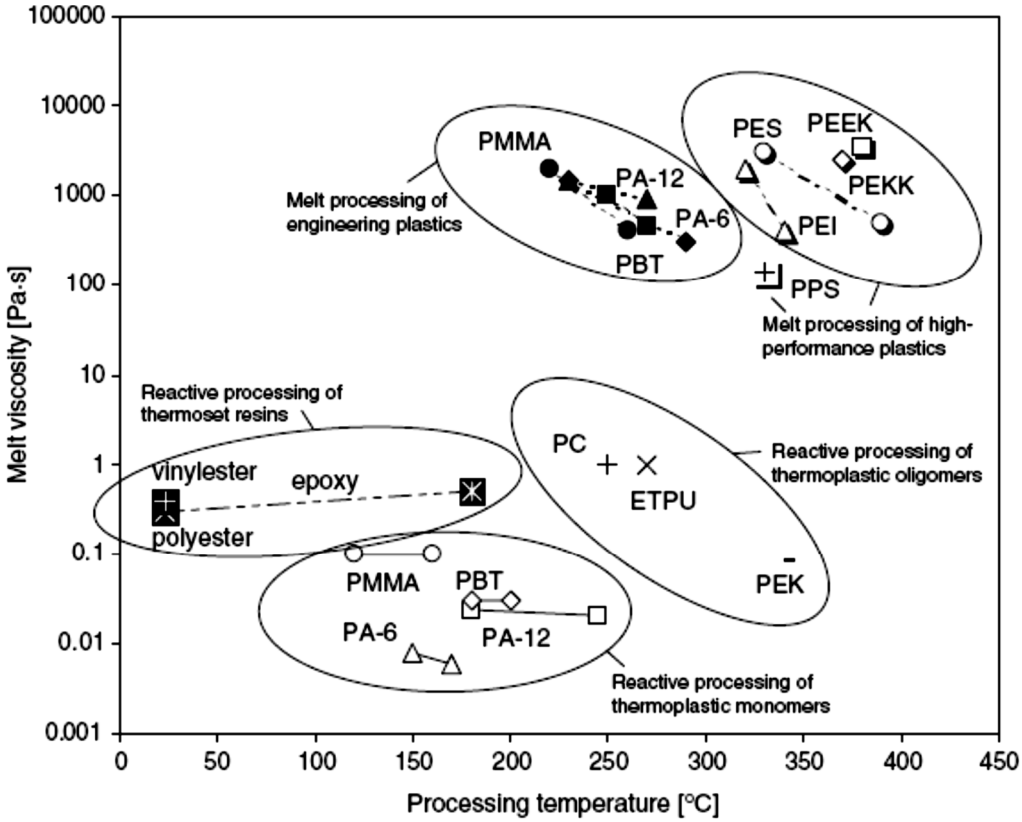


Figure 2.16 : Melt viscosities and processing temperatures of various matrix materials for both reactive and melt processing [15].

Processing of reactive thermoplastics

Three reactive thermoplastic materials in particular are known to be developed which can be processed to produce composites, caprolactam, APLC-12 and Cyclic PBT. In both cases, the resin is a pre-activated monomer melt with low viscosities, which polymerises in-situ to form tough, solvent-resistant, semi-crystalline polymer matrices. Fiber reinforced composite production by liquid molding of these thermoplastics has received renewed attention due to the development of both the liquid activator system for the APLC and the commercialisation of cyclic oligoesters. The biggest difference with thermoset RTM is the higher processing temperatures above the precursor's melting point.

An important advantage of the reactive TP method is that the processing can be carried out at near-isothermal conditions, i.e. the material solidifies and crystallises at the processing temperature. It is not, therefore, necessary to cool the tool in order to de-mold the component, which is an important economic consideration, leading to energy savings and shorter cycle times. The combination of low viscosity and rapid polymerisation of CBT resin allows for fast processing in many different applications. In addition, the initial water-like viscosity allows rapid and excellent wet-out of filler

reinforcements and high filler loadings can be achieved at large scale component processing. This behavior is due to the fact that the Cyclics resins polymerise at temperatures below both the melt temperature and the crystallization temperature of the PBT polymer [15, 16]. For application of cyclic resins infusion system including, heatable mold, vacuum pump and resin and activator infusion pump as shown Figure 2.17 can be used [15, 42].

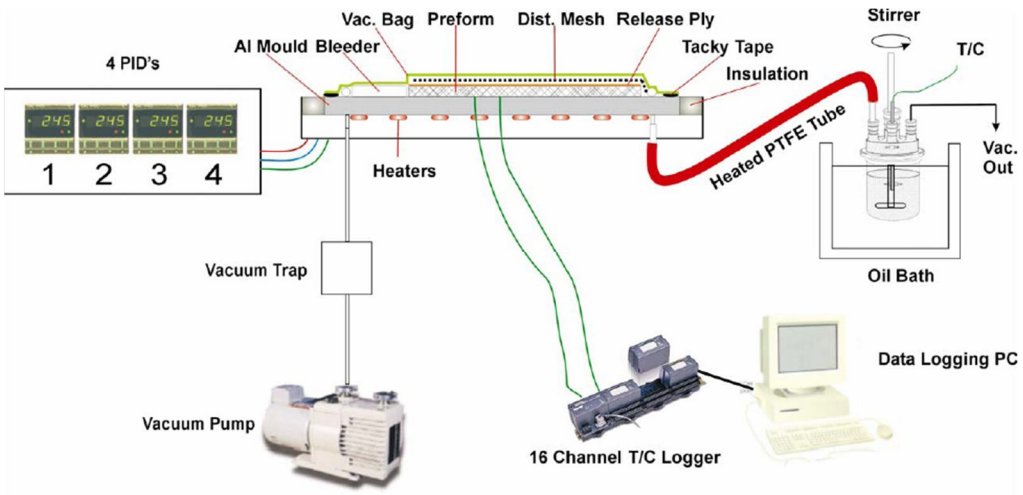


Figure 2.17 : Vacuum assisted resin infusion process [15].

J. Lohmiller and S. J. Winckler worked on RTM processing of one part CBT system where the catalyst is pre-combined with the resin since there are few processes that can effectively mix a reactive catalyst at ratios approaching 200:1 by volume. The basic idea is similar to that of a hot glue gun, as shown in Figure 2.18, where solid resin is placed in a warm cylinder(140°C), and a piston is used to move the resin and force it against the heated end plug, which is much higher in temperature (230°C).

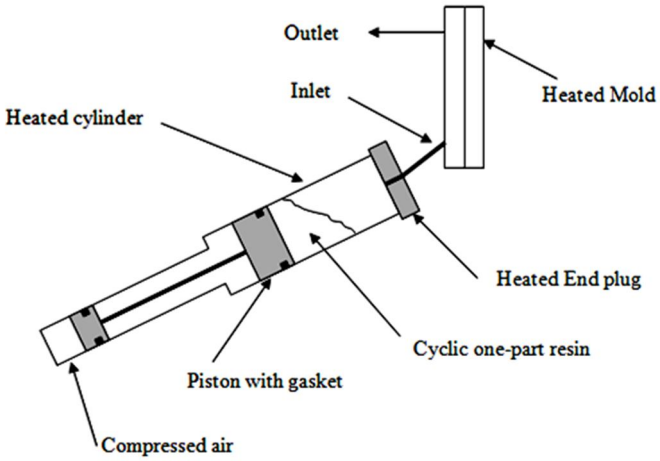


Figure 2.18 : RTM setup for cyclic one-part resins [43].

In this process the mold temperature is an important parameter. Increasing the mold temperature will speed polymerisation, but as the melt point of PBT is approached the subsequent crystallization will be slowed. At the melt point of PBT (225°C) and above, the polymerisation will be rapid but the material will never crystallize and solidify until it is cooled below 225°C. As a baseline, the optimum (fastest) isothermal temperature is in the 190°C range as a compromise between polymerisation and crystallization. This goes for both the fast titanium base catalyst system as well as the slower stannoxane based catalyst system; with de-mold times in the 10 and 30 minute range respectively. Cycling the mold temperature up to 225°C for example, to promote rapid polymerisation, followed by cooling to 190°C to promote rapid crystallization, solidification, and de-molding, can improve the molding time of titanium catalyst from 30 minutes down to the 10-15 minute range, a substantial reduction. In all part production, the system (mold and enjector) has to be covered with a mold release and has to be cleaned before start to molding [43].
In the liquid molding processes (e.g. RTM, Vacuum inf.) of CBT, the main issue is the time window (time to reach 1 Pa.s.) for successfull impregnation of the fibers. CBT oligomer mixture has a melt viscosity of 150 mPa s at 150°C, which drops to 30 mPa s at 190°C. When processed at 190°C in protective atmosphere, the viscosity reaches 1 Pa.s after approximately 5 minutes and final conversions of 95–99% are obtained within 30 min. The impregnation time varies from seven (180°C) to two minutes (220°C) depending on the polymerisation and thus mold temperature. Due to the narrow impregnation time processing parameters have to be controlled to achieve fully impragnated final part [23, 42, 43].

Both nylon 6 and 12 can be polymerised through two processes, condensation polymerisation and anionic ring-opening polymerisation. The condensation polymerisation of Nylon 6 and 12 are common commercial methods to produce the polymer, but both have byproducts, such as water, that make them unacceptable for RTM applications. On the other hand, anionic polymerisation of lactams 6 and 12 (2) can produce nylon 6 and 12 respectively, with no byproducts, and within times acceptable to the RTM process. Anionically polymerised lactam 12 (APLC-12) is currently marketed by EMS Chemie A.G., Switzerland, who also developed a one part activator–initiator solution called Grilonit that can be stored indefinitely in inert atmosphere. APLC-12 materials are processed at molding temperatures between 180° C and 240° C, and the polymerisation time varies from seconds to minutes, depending on the percentage of activator used, and is shorter at higher temperatures. Viscosities less that 0.1 Pa.sec can be achieved with APLC-12

molding, and as a result, infiltration of high fibre volume-fractions under gravity forces only has been demonstrated. The polymerised composite must be cooled to below 100° C before de-molding, See Fig. 2.19.

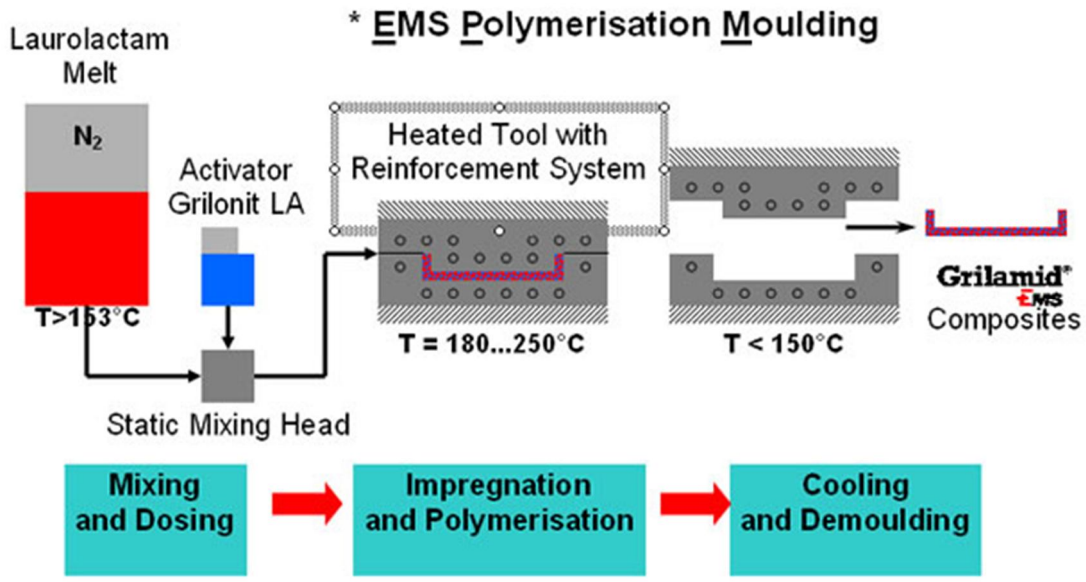


Figure 2.19 : Liquid-Molding of laurolactam [31].

Liquid molding process can also be used for anionic polymerisation of polyamide-6 (PA-6), no longer requires pre-mixing of two separate material batches that slowly polymerise over time (60 minutes at 180°C). A vacuum infusion process for manufacturing of polyamide-6 (Nylon 6) composite wind turbine blades is currently being developed at The Delft University of Technology. The difficulties of processing of anionically polimerized amides is the sensitivity of the polymerisation process to moisture and oxygen which can cause poor matrix properties due to low conversions and possibly a relatively high void content (15%). In this process to avoid moisture, a well equipped tooling is necessery as follows: a heated tank storing monomer above its melting temperature under a nitrogen environment which is connected to a gear pump which injects the monomer to the mixing head via a oil-heated hose; a second tank storing the liquid activating system connected to another gear pump, injecting the liquid system to the mixing head via a water cooled hose. Tanks and hoses ensure a perfect insulation of both materials to ambient air, preventing any reaction pollution. The monomer and the liquid activating system are brought in contact in the mixing head thus initiating the polymerisation just prior to injection [37, 38].

The drawbacks to both nylon systems include material properties and processing complications. The processing both systems are very sensitive to water and impurities (including fiber sizing) during the polymerisation process. Small amounts of water (in the few ppm range) can have adverse effects on polymerisation and few standard fiber-sizing packages are compatible. In structural composites, one of the important properties for structural applications is the modulus of the matrix material, needed to properly support fibers in compression. Micromechanics models and test data both show lower compression strength with lower modulus. The modulus of nylon 6, in the range of 2.8 GPa, approaches some epoxies, but this is the “dry” as-molded modulus. After conditioning at room temperature in 50% relative humidity, the modulus will drop to less than half of the “dry” value. Such a variable modulus is difficult to deal with from a design point of view, and leads to a wide specification with additional weight and cost. The moisture absorption of nylon 6, which can go above 5% by weight, also causes dimensional stability problems, including warping and interference problems of components during operation. Nylon 12 in comparison has very low moisture absorption and will be stable in a varying humidity environment, but it does have a lower modulus than nylon 6 to start with. A more attractive thermoplastic material would combine the low moisture absorption of nylon 12 with the modulus of “dry” nylon 6 [43].

2.5 Cyclic Butylene Terephthalate

2.5.1 Production of cyclic oligoesters

Polyester is typically manufactured by two routes: transesterification of dimethylester with diol to form an intermediate diester and oligomers, followed by polycondensation to form the polymer; or direct esterification of the diacid with the diol, followed by polycondensation. Conventionally Produced polyesters contain small amounts (%4-5) of cyclic low molecular weight oligomers. These oligomers can create problems during PET fiber processing, such as spinning and dyeing. They can usually be extracted from the polymer product by the Soxhlet extraction method using several solvents like chloroform, dioxane, dichloromethane or xylene [44-45]. They can also be removed with dissolution methods. The polyester is dissolved in a solvent, such as phenol and tetrachloroethane mixture, dimethyl formamide, or 1,1,1,3,3,3-hexafluoro-2-propanol. The solution is filtered off and evaporated to obtain dry oligomers. Cyclic oligomers removal is not currently practiced in industry [46]. Usually only small amounts of cyclic oligomers are formed during bulk condensation polymerisations, but cyclic oligoesters can be prepared as

major products by using very high dilution conditions, polymer-supported techniques, and cyclo-depolymerisations (ring-chain equilibrium reactions). The synthetically produced cyclic oligoesters have been reported to have physical properties similar to the cyclic oligomers extracted from condensation polymers. These cyclic oligomers can be used as feedstock for ring-opening polymerisation [47].

2.5.1.1 Direct synthesis

Cyclic oligomers have been prepared by a classical high dilution technique. It is a simple reaction at high dilution of: (a) diol and diacid, (b) diacid and diester, or (c) diester only. A novel pseudo-high dilution condensation reaction has been developed for preparing cyclic oligomeric alkylene phthalates and. The pseudo-high dilution condensation reaction allows high product concentrations and produces larger quantities, since large volumes of solvent are not necessary. The reaction is carried out by using a diol (HO–A–OH) or one bis-(hydroxyalkyl) ester with one diacid chloride (Cl–CO–B–CO–Cl) in the presence of highly sterically unhindered amines such as 1,4-diazabicyclo[2,2,2]octane (DABCO) or a mixture thereof with a tertiary amine, such as triethylamine or pyridine [47].

2.5.1.2 Polymer-supported method

Cyclic oligomers can be prepared by using polymer-supported reagents. It was reported that cyclic polyester was prepared by the utilization of an intramolecular alkylation reaction of a ω-bromocarboxylic acid using an anion-exchange resin [48].

2.5.1.3 Cyclo-depolymerisation (ring-chain reaction)

Cyclic oligomers can be obtained by the cyclo-depolymerisation (CDP) of linear polyesters, and this technique is also useful for recycling of polyesters. A typical depolymerisation is carried out by refluxing in dilute solution for many hours in the presence of metal catalysts, such as organotin or titanate compounds. Different solvents and catalysts were used for the depolymerisation at low concentrations. At the end of the reaction, the solution is cooled down to a certain temperature at which point the polymer is precipitated [49-51].

2.5.1.4 Production of CBT oligomers

Brunelle and his co-workers found a route to making cyclic form of PBT. Using conventional PBT production techniques, a small equilibrium concentration of low molecular weight cyclic oligomers are formed within the predominantly linear polymer. Interestingly the cyclic form, when isolated and melted, has a viscosity as low as 17 m-Pascal-seconds (17 centipoise), a water-like viscosity. This equilibrium

between linear and cyclic forms of PBT is driven by entropy, and is concentration dependent. The equilibrium can be driven to favor cyclic formations by lowering the overall concentration in a solvent. The basics of the cyclic technology are to use high dilution of normal PBT with a catalyst to drive the conversion to the cyclic form, then isolating the cyclic oligomers by removing the solvent. The resulting cyclic form of PBT (CBT) is solid at room temperature, white in color, with a melting range of 120°-160°C. Cyclics Corporation produces commercial cyclic oligomers of butylene terephthalate (CBT), as a mixture of dimer, trimer, and tetramer via the degradation of PBT [42, 52].

2.5.2 Polymerisation of cyclic oligoesters

Many studies on conversion of cyclic oligomers to high molecular weight linear polymer via ring opening polymerisations have been presented. It was concluded that the ring-opening polymerisation offers potential advantages relative to the conventional polymerisation process. Higher polymer molecular weights can be more easily achieved. Molecular weights as high as 100,000–300,000 g/mol were reported for ring-opening polymerisations, while the highest molecular weights achieved by step polymerisation are 40,000–60,000 g/mol. Additionally, there is no by-product in the ring opening polymerisations. The low melt viscosity of the cyclic oligomers also allows processing by various techniques, such as pultrusion, resin-transfer molding, melt filtration, or reaction injection molding, either concurrent with or just prior to polymerisation (Fig 2.20). Low viscosities are thought to be very useful for producing polyesters with high melting points and high melt viscosities, such as PEN or poly(butylene 2,6-naphthalate) (PBN) [15, 52].

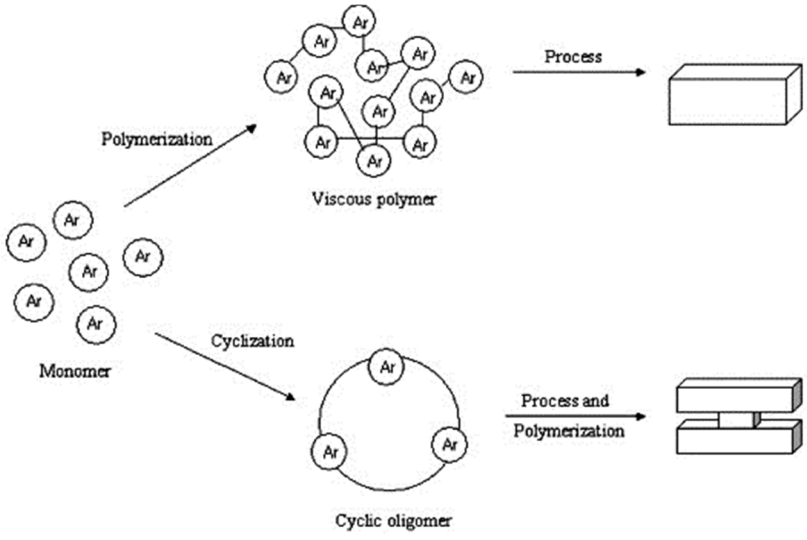


Figure 2.20 : Conversion of monomers to low viscosity macrocyclics (bottom) conventional polymerisation (top) forms viscous polymers [52].

Brunelle and his coworkers, reported that the PBT cyclics melted at much lower temperatures, softening at 140 °C and being completely molten at 160–190 °C. Again, the advantage of a mixture was seen, since pure cyclic dimer melts at 196°C. The molten cyclics had a very low viscosity (about 30 cP at 190 °C), and could be easily stirred in a flask with a magnetic stirrer, making melt polymerisation studies facile. Ideally, they tried to polymerise the PBT cyclics below the melting point of the final polymer (~ 225 °C), so that thermal cycling during processing would not be necessary. Initially, some difficulties with low temperature polymerisaton (< 200 °C) were encountered, with either slow or incomplete polymerisation being observed for the cyclics prepared at large scale. After careful analysis, they found that the presence of either carboxylic acids or carboxylic anhydrides could inhibit the polymerisation at low temperatures. The high levels of water that had plagued us during synthesis also affected polymerisation. Polymerisation at higher temperatures (250 °C) was possible, but not as desirable, especially since these impurities would also limit the ultimate molecular weight achievable. Ultimately, they found that stirring CH_2Cl_2 solutions of the cyclics with silica gel adsorbed the undesirable imprutities, and gave PBT cyclics which polymerised normally [42,52].

Many catalysts have been used for polymerisation of polyesters via condensation, and many of these worked quite well for cyclics polymerisation (Table 2.6). The two classes of catalysts that proved most efficient were titanium alkoxides and cyclic stannoxanes, both of which work by a coordination-ligand exchange mechanism. The mechanism of the polymerisation is similar to conventional ROP, with initiation and propagation steps [Figure 2.21]. However, because the large oligocyclic rings have essentially no ring strain, there is no detectable exotherm upon polymerisation.

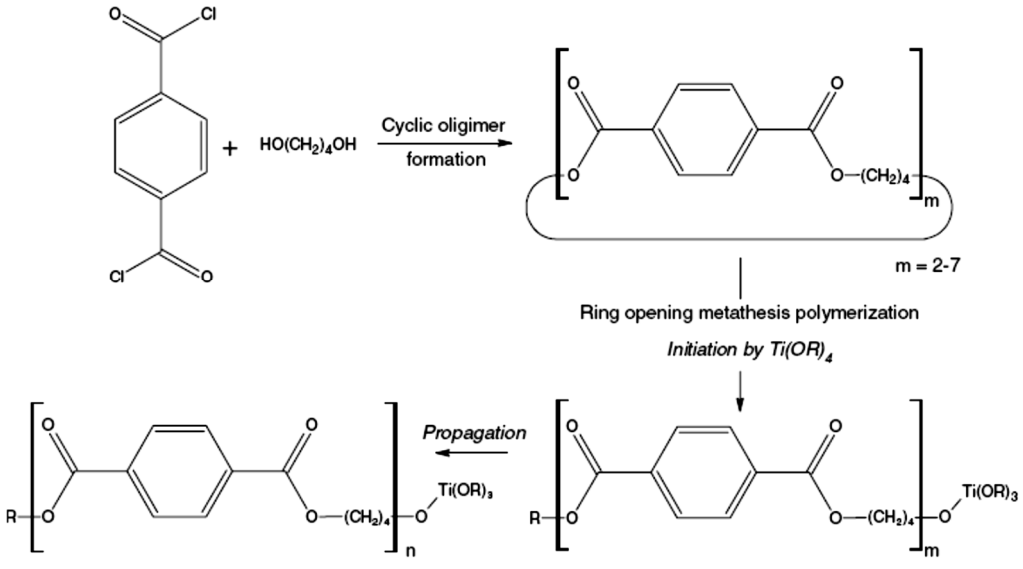


Figure 2.21 : Ring-opening metathesis polymerisation of PBT[15].

Table 2.6 : Catalysts (initiators) used in polymerisation of CBT.

Initiator (mol %)[b]	Temperature (°C)	Time (min)	Polymerisation (%)	$M_w \times 10^{3}$[c]	M_w/M_n
Bu_2SnO	275	10	97	58.9	2.5
$Ti(O\text{-}i\text{-}Pr)_4$ (0.2)	190	6	98	115	2.1
TOT (0.1)	190	20	99	352	2.1
TOT (0.2)	190	20	98	117	2.25
TOT (0.3)	190	6	96	95	2.8
TOT (0.3) + 1.0% linear[d]	190	106	95	61.2	2.8
Stannoxane 1 (0.05)	190	20	91	401	1.3
Stannoxane 1 (0.4)	190	20	95	330	1.9
NaOEt (1.0)	225	10	41	5.3	ND
$Sn(OMe)_2$ (1.0)	250	10	54	36	ND
Comm PBT[e]	NA	NA	98	111	2.3

a Polymerisations were carried out by adding initiator in minimum solvent to molten cyclic PBT at the temperature shown.
b Mol % relative to monomer units.
c By GPC versus polystyrene standards.
d Bis(4-hydroxybutyl) terephthalate was added as linear.
e Sample of commercial Valox 315.

Since the polymerisation is thermo neutral, chain-transfer reactions take place at the same rate as ring-opening reactions, and thermodynamic equilibrium is achieved, affording polyester with polydispersivity of about 2.0. Because the end groups are provided only from the initiator, the ultimate molecular weight depends on the initiator level; alternatively, molecular weight can be controlled with added alcohol. The cyclic stannoxane initiator is interesting, in that it provides no end groups. The tin alkoxide functionality becomes built into the polymer, which is a very high-molecular-weight macrocycle (Figure 2.22) [42, 47, 52].

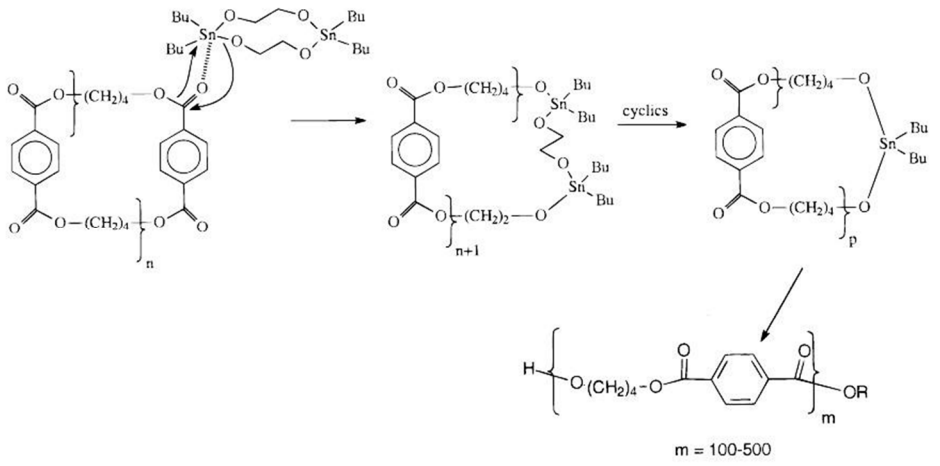


Figure 2.22 : Incorporation of tin into a macrocyclic structure via cyclic stannoxane [52].

In order to drive the polymerisation of CBT into PBT, catalysts based on tin or titanium are used with concentrations in the range of 0.1 to 0.5 molar percent. Titanium based catalysts (e.g. tetrakis (2-ethylhexyl) titanate “TOT”) are among the fastest but can be very moisture sensitive, while tin based catalysts (e.g. stannoxane) tend to be somewhat slower but can be insensitive to moisture before polymerisation. All CBT/catalyst combinations need to be dry before the polymerisation. The processing temperature can be from the melt point of 160°C up to 250°C where PBT begins to degrade, with polymerisation rate increasing with temperature. Of the three main process variables controlling the rate of polymerisation (temperature, catalyst type, and catalyst concentration), catalyst concentration is least often used because increasing the catalyst concentration leads to lower molecular weight PBT (more sites for polymerisation lead to smaller molecules), and lowering the concentration starts to effect the robustness of the process. Therefore the catalyst concentration is often fixed for each particular catalyst, and process optimization focused around temperature and catalyst type. Temperature can have a very strong effect where, for example, a slow catalyst that takes 30 minutes for polymerisation at 190°C may take only 1 minute at 250°C [43, 47].

Isothermal polymerisation

If the CBT resin is polymerised at 190°C, for example, then the material will melt, polymerise, and then crystallize and solidify without cooling. This is because the process temperature, 190°C, is below the melt point of the PBT polymer created, which is in the range of 225°C. This is a very important attribute of the CBT system that can allow for rapid processing in a thermoset-like manner.

2.5.3 Properties of CBT and IPCBT

2.5.3.1 Viscosity

Commercial CBT pre-combined with catalyst in the ratio of 200:1 by volume, namely one-part CBT systems, is stable at room temperature in solid form, and will begin to polymerise upon melting. Two systems that rely on tin based catalysts are XB3 which uses a transeterification catalyst from Autofina, FASCAT 4101, and XB2 which is based on stannoxane.

The complex viscosity of the cyclic PBT can be observed through the entire polymerisation process using an oscillating parallel plate test [43]. Figure 2.23 represents rheokinetic data for both systems, XB and XB2. The comparison of XB3 at 170° and 190°C shows the strong effect of temperature, with the 190°C curve

reaching 1 Pa-s viscosity in 140 seconds compared to 500 seconds at 170°C. The comparison of catalyst types, in one-part resins XB2 and XB3, at 190°C show dramatic differences, with the XB2 curve reaching 1 Pa-s viscosity in 50 seconds compared to 140 seconds for the XB3 system.

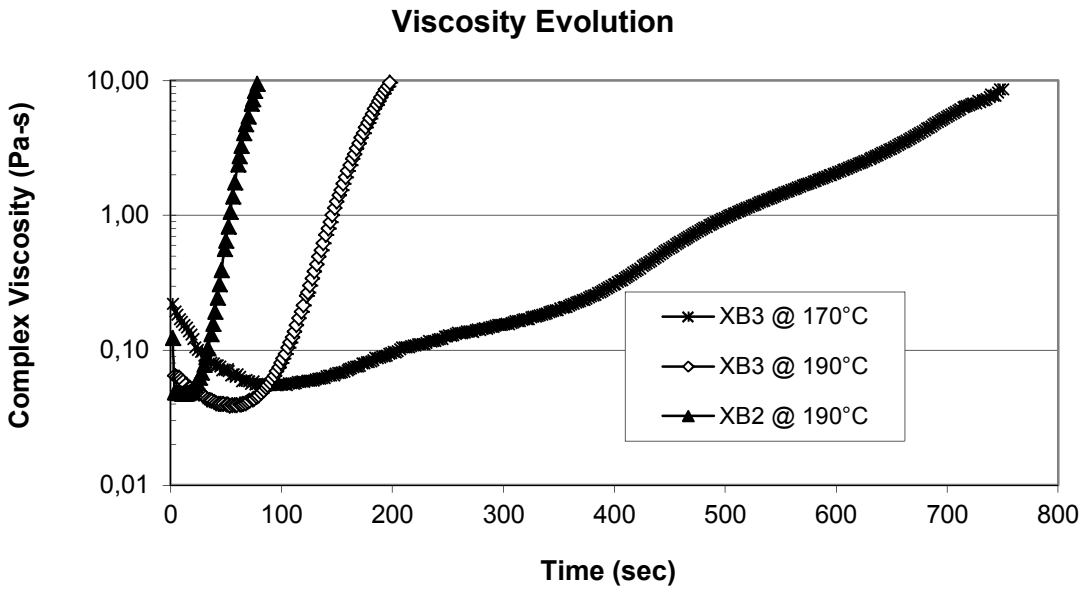


Figure 2.23 : Rheokinetic plots of CBT one-part systems XB2 and XB3 [43].

It is clear that at higher temperatures, the reaction, and hence the viscosity rise, proceeds more rapidly. This causes decreasing in needed time for impregnation of the fibers. (time to reach 1 Pa.s). This needed time range can enlarge by keeping the process temperature low. However, low process temperatures increase the polymerisation time (see Figure 2.24).

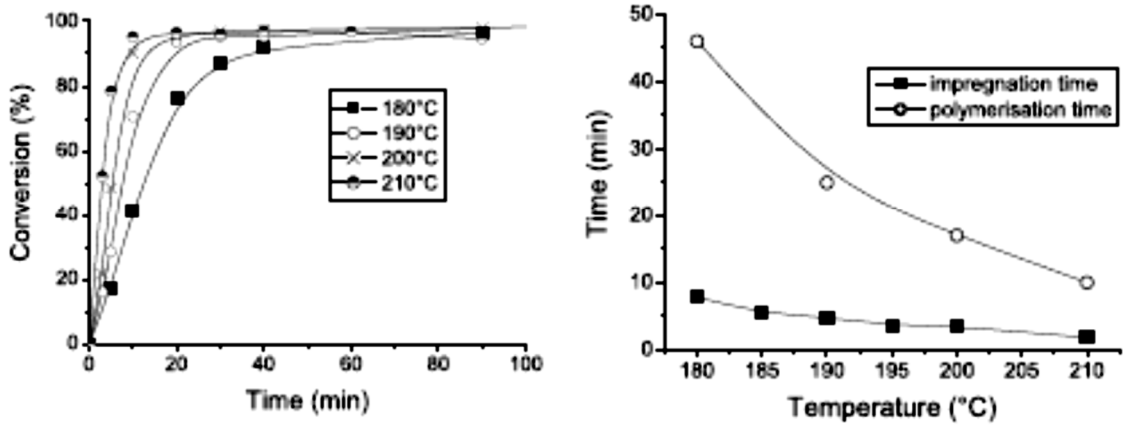


Figure 2.24 : Left: Degree of conversion as function of time for different temperatures; Right: Impregnation and polymerisation time of the one-part CBT(CBT-XB3) resin [23].

2.5.3.2 Morphology

PBT is well known to be among the easiest of the semi-crystalline polymers to crystallise. This makes PBT difficult to produce amorphous structures unless specimens are very thin and quenching is very rapid. PBT has a triclinic unit cell for both known polymorphs, α being the predominant polymorph, whereas the β polymorph is only observed in drawn and spun fibers [53]. It was observed that there is an increase in amount of usual type spherulites when the cooling rate decreased and the melt temperature increased [54].

At a low rate of crystallisation and small degree of under-cooling (where crystallisation takes place at temperatures above 180°C), the crystallisation of linear PBT resulted in the 'usual' spherulites. While, below the temperature of 180°C, at which the highest rate of crystallisation occurred, 'unusual' 18 spherulites will be formed. However, it is found that cyclic PBT, produced by isothermal polymerisation and crystallisation at 190 °C, is composed only of the 'usual' spherulites [55]. They are small (approximately 2-3 μm diameter) and appear to be produced by very rapid crystallisation. This suggests that cyclic PBT crystallises easily and there are clear differences in kinetics compared with linear PBT. This behaviour is not fully understood and is further complicated by the fact that for the cyclic PBT, crystallisation and polymerisation are taking place at the same time. Together with the increasing amount of usual type spherulites, PBT became more brittle, reducing the strain at failure from more than 30 to less than 4% [54, 55].

Depending on the degree of supercooling and the reaction speed, isothermal processing of CBT may result in simultaneous polymerisation and crystallization. Simultaneous polymerisation and crystallization can lead to a very different crystal morphology ranging from a fully extended chain conformation to a folded chain conformation, which is the typical conformation for crystallization from the melt [56].
Fig. 2.25 shows the degree of crystallinity as function of time for catalyzed CBT oligomers. Before crystallization can commence, these oligomers need to convert to polymer of sufficiently high molecular weight.

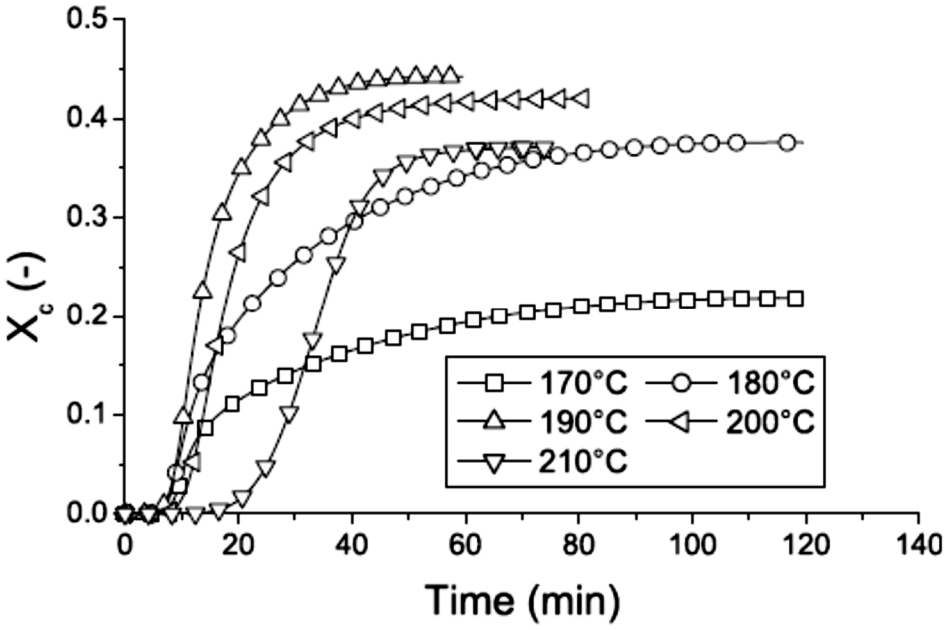


Figure 2.25 : Crystallization kinetics of catalyzed CBT resin [19].

Crystallization curves of melt crystallized PBT usually show a decrease in crystallinity and an increase in crystallization speed when the degree of supercooling increases [57, 58]. If polymerisation and crystallization were consecutive, meaning that molecular weight build-up was completed before the start of crystallization, the crystallization kinetics would not differ from meltcrystallized PBT, except for a time-shift equal to the time needed for polymerisation. Since the crystallization curves presented here clearly differ from melt crystallized PBT, it can be concluded that for temperatures below 200°C, where polymerisation is relatively slow, polymerisation and crystallization are simultaneous. As mentioned before, this simultaneity can affect the crystal structure, the final degree of crystallinity and hence the mechanical properties.

Typical stress–strain curves are depicted in Figure 2.26. which represents the flexural tests performed on pCBT, isothermally processed at 190ºC, pCBT polymerised at 230ºC and crystallized at 190°C and classically produced PBT (rapid cooling from the melt). It is clear that the pCBT behaves differently from PBT. Apart from the higher modulus, pCBT breaks in a brittle manner whereas the PBT samples do not break at all in this three point bending test, but show a yield point.
The difference between simultaneous (at 190°C) and consecutive (at 230°C) polymerisation and crystallization is smaller but still obvious. Although both samples are brittle, breaking at small strain levels, the samples prepared by consecutive

polymerisation and crystallization at 230°C do exhibit higher strain to failure and higher strength of sufficiently high molecular weight [19].

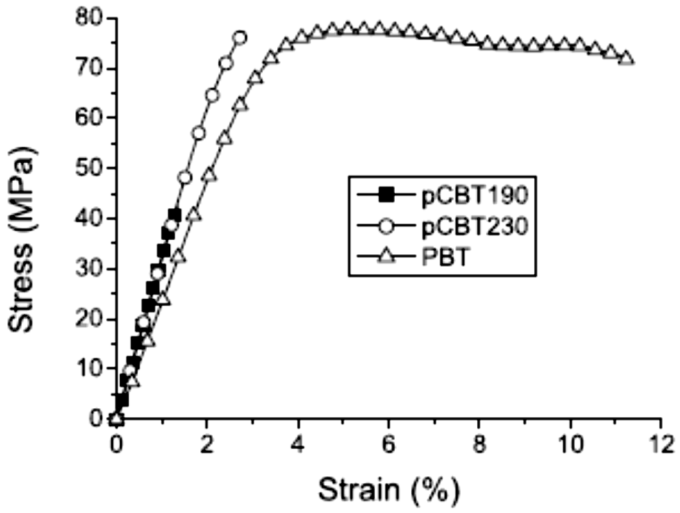


Figure 2.26 : Typical three point bending Stress-Strain curve of pCBT and PBT[19].

DSC diagrams show that thermal behaviour of CBT, polymerised CBT(ISP-PBT), and injection molded commercial PBT (IM-PBT) [18].

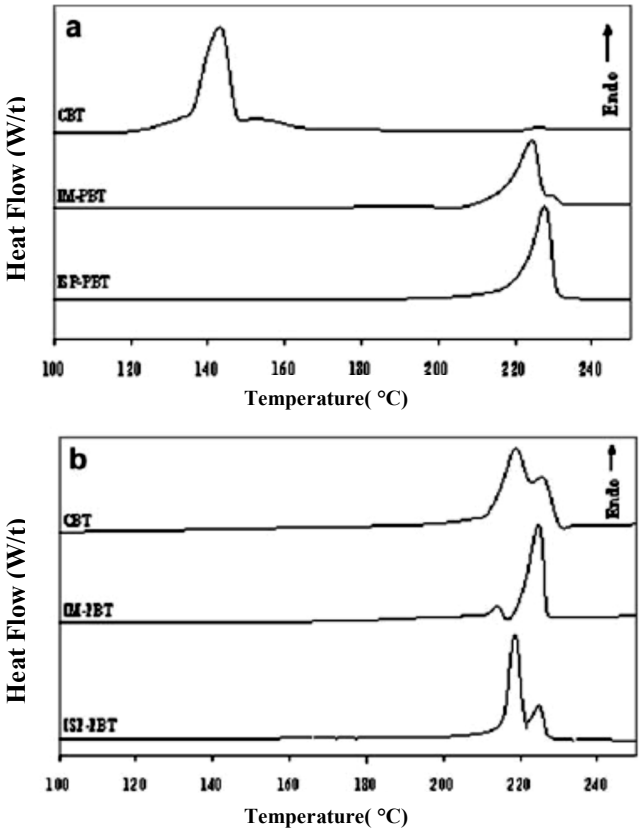


Figure 2.27 : Thermograms of CBT, ISP-PBT and IM-PBT: a)first b) second heating (heating rate: 5°C/min) [18].

It can be seen that CBT melts in a broad range (from about 120 to 170°C). The broadening of the shoulder may be ascribed to the different melting temperatures of the oligomers present in the CBT. It was reported that the heating rates play an important role in detecting the exothermic process (mostly related with the crystallization) during the first heating of CBT. The slower heating rate allows the polymerised CBT to crystallize and melt subsequently inside the DSC pan. So, high DSC heating rates hinder the crystallization of the PBT produced and as a consequence its melting peak is missing, too [18]. In another study, modulated DSC (MDSC) was used to study the polymerisation of a CBT as a function of the end temperature (T = 200 and 260°C) and holding time. The melting behavior of the PBT was strongly affected by the polymerisation mode (performed below or above the melting temperature of the PBT) [59].

2.5.3.3 Mechanical properties

Table 2.7 shows the tensile and flexural properties of commercial injection molded PBT (PBT) and polymerised CBT (IPCBT) at 190°C for 30 minutes. It can be seen that both types of PBT possess similar values of strength and stiffness. However, the relatively low tensile strain of ISP-PBT indicates its brittle nature.

Table 2.7 : Mechanical properties of PBT and IPCBT [18].

	Density (g/m3)	**Tensile Stregnth (MPa)**	**Tensile Modulus (GPa)**	**Tesnile Strain(%)**	**Flexural Strength (MPa)**	**Flexural Modulus (GPa)**
PBT	1.30	56	2.4	8.0	112	2.3
IPCBT	1.32	59	2.3	2.3	104	2.4

In another work, it was reported that reprocessed polymerised CBT, injection molded CBT and PBT gaved close strength and modulus values, but different strains indicating its high crystalline nature, represented in Table 2.8.

Table 2.8 : Properties of reporcessed PBT and polymerised CBT compared to injection molded polymerised CBT [19].

	Tensile Stregnth (MPa)	**Tensile Modulus (GPa)**	**Tensile Strain(%)**
RP-pCBT	46	2.3	3-70
RP-PBT	50	2.5	16-225
IM-pCBT	55	2.4	160

3. MATERIALS AND METHODS

3.1 Materials

The main focus of this chapter is to develop prepregs and to produce their composites. For this purpose all materials and the all prepreg and composite production methods were described detailed.

3.1.1 Reinforcing materials

E-Glass fibers in different yarn numbers (tex) were received from Şişecam Cam Elyaf San. A.Ş. Chemical structure is E-Glass composition consisting principally oxides of; silicon, aluminum, calcium, boron, including sizing compound on surface such as complex mixture based on silanes, polymers and polyester resins as a coupling agent. Used fibers are compatible with unsaturated polyester resin for thermoset composite applications. Properties;

Melting Point: 840°C(pertains to bare glass)

Specific gravity: 2.6 g/cm³ (pertains to bare glass)

Number of tex (g/1000 meter), used are 300 tex, 600 tex and 68 tex.

Diameter of fibers:14 µm for 300 tex, 15 µm for 600 tex

Reinforcements were provided by Metyx Composites®. For manufacturing of pre-pregs, 2 types of biaxial 1 type of unidirectional non-non-crimp reinforcement were used. Glass fiber biaxial reinforcements have been produced on 2 axes consisting two layers on +45°/-45°. The biaxial coded as X600 (Figure 3.1) has 600 g/m² areal weight and includes 2 layers of fiber on +45°/-45° axes. 1 layer is consisting 50% of 300 tex, 50% of 600 tex glass fiber with 300 g/m² areal weight. Fiber mixing was preferred to eliminate the gap formation between fibers and to take advantage of different fiber diameters such as high tensile strength of 600 tex, high flexural strength of 300 tex due to the increased surface area. The biaxial coded as X468 has areal weight of 468 g/m² (Figure 3.2) and includes 2 layers of fiber on +45°/-45° axes consisting 300 tex fibers with 234 g/m² areal weight for each layer.

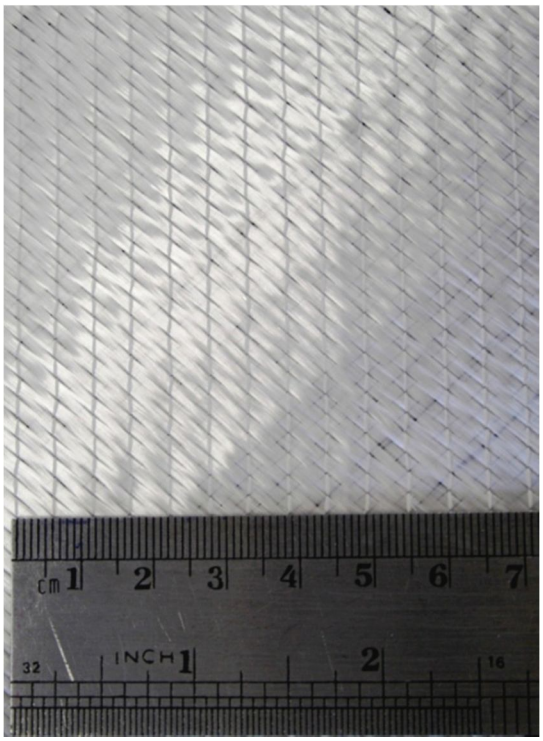


Figure 3.1 : Representation of X600 coded ±45° reinforcement.

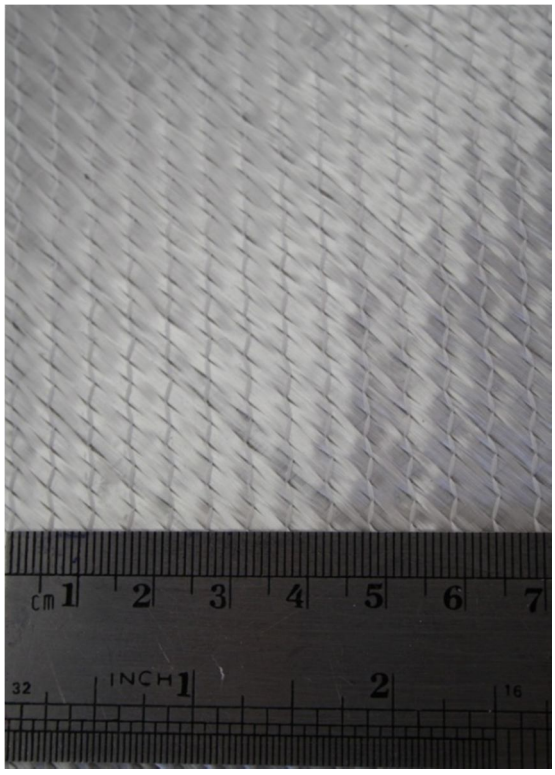


Figure 3.2 : Representation of X468 coded ±45° reinforcement.

Unidirectional reinforcement coded L300 (Figure 3.3) consists of 600 tex glass fiber on 0° axis. Glass fibers in all reinforcements were hold together by means of stitching with a polyester yarn.

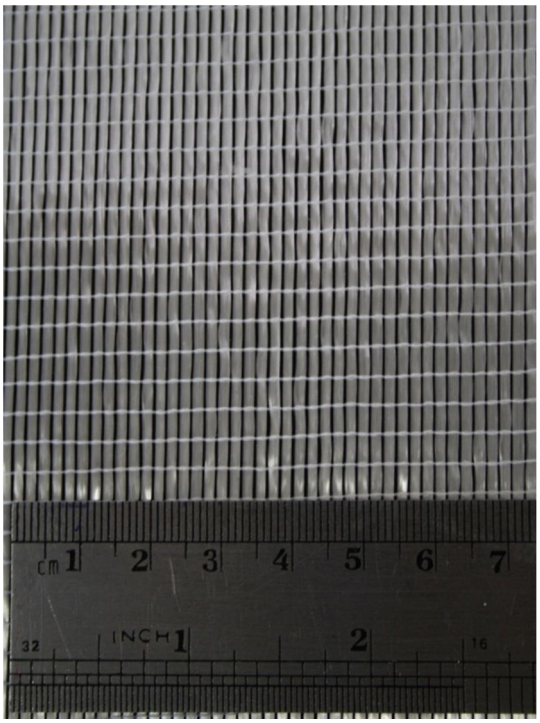


Figure 3.3 : Representation of L300 (UD) coded reinforcement.

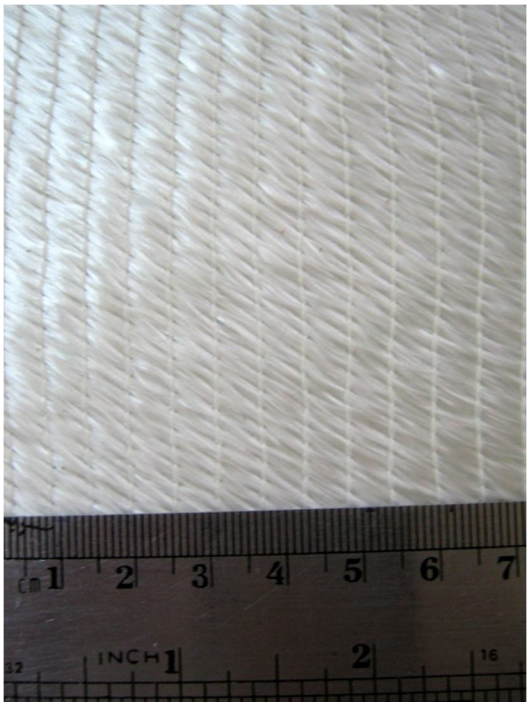


Figure 3.4 : Commingled Glass/PBT hybrid biaxial (±45°) fabric.

Commingled Glass-PBT hybrid fabric was provided by Metyx Composites ® (Figure 3.4). The fabric in weight of 750 g/m² is coded as TPX750 PBT in which each layer of +45°/-45° includes 100% of 300 tex glass fiber. The Glass/PBT weight ratio is 60/40.

3.1.2 Matrix resins

3.1.2.1 Cyclic butylene teraphthalate

CBT (Cyclic poly(1,4-butylene teraphthalate) including stannoxane as a polymerisation catalyst was obtained from Cyclics Corporation (CBT160).

Properties of the resin;

Polymerisation Molecular Weight: >100,000 g/mol

Bulk Density (as pellets): 0.7 g/cm³

Specific gravity 20°C (solid): 1.3 g/cm³

Melting Range: 120—200 °C

Viscosity (200°C): 20mPa·s

3.1.2.2 Polyamide 12

Polyamide 12 was obtained from EMS Chemie AG in powder form (EMS Griltex D 1428A).

Properties of the resin;

Bulk Density (as pellets): 1.01 g/cm³

Melting Range: 175—180 °C

Viscosity (230 °C/2.16 kg): 210 Pa·s

3.1.2.3 Copolyamide (CoPA) suspension

Copolyamide suspension was is obtained from EMS Chemie AG in suspension form (CoPA suspension 2A)

Properties

Bulk Density (as pellets): 1.02 g/cm³

Melting Range: 120—130 °C

Viscosity (160°C/2.16kg/dried): 600 Pa·s

Particle size distribution;

D (v, 10%) µm 0.4

D (v, 50%) µm 0.6

D (v, 90%) µm 0.9

Properties of this polymeric suspension in water;

• Solid content of 40% by weight

• Average particle size < 1 µm

Benefits of the suspension is;

• Good penetration into dense fabrics and yarns

• Increase of chemical resistance

• Increase of impact resistance

3.1.2.4 Unsaturated vinyl ester

Unsaturated vinyl ester resin namely Crystic VE-676-03 was supplied by Scott Bader Co. Ltd. The resin solution includes 50% of styrene giving a viscosity 175 ± 25 mPa.s with Brookfield viscosimeter at 25°C.

3.1.3 Other chemicals

3.1.3.1 Semi permanent mold release agent

Release agent was obtained from AXEL Plastics. Agent is a proprietary resin solution comprising modified siloxane-based polymers which crosslink and form a release film upon evaporation of the solvent carrier. Application temperature is up to 60°, use temperature is up to 210°C.

3.1.3.2 Dicumyl hydroperoxide (DCP)

DCP was used as catalyst for curing of unsaturated vinyl ester resin.

3.2 Equipments

3.2.1 Weighing machine for hand scattering

TEM- NT3 model balance which has 3000 gr weighing range, 0,1 g readability (was used to prepare pre-pregs scattering of powder with hand by means of a metal screen in Figure 3.5.

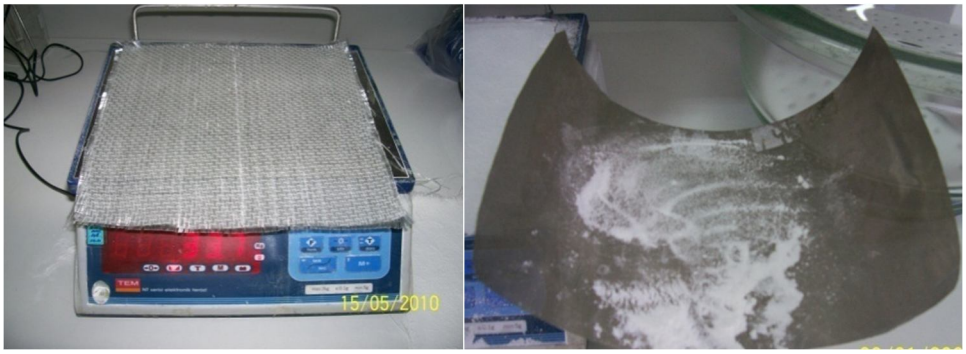


Figure 3.5 : Weighing machine (left) and metal screen for scattering (right).

3.2.2 Scattering coating machine

Scatter coating machine was used for scattering CBT powder on reinforcement and fixing CBT onto fiber surfaces by heating and melting. This machinery system has a scattering unit and 2 m long oven heated by infrared beams. The conveyor band a maximum rate of 60 m/min. and it can be heated to a maximum temperature of 250°C (Figure 3.6).

Figure 3.6 : Scattering part of scattering coating machine.

3.2.3 Fluard machine

Laboratory scale fluard was used to impregnate the suspension CoPA to glass reinforcement. The machine has a liquid bath with 1000 ml capacity and the squezzing rubber rollers of the excess of the liquid. The rollers have max. 4 bar pressure and max. 10 rpm turning speed (See Fig. 3.7.).

Figure 3.7 : Fluard machine.

3.2.4 Oven

Nüve FN400 model laboratory oven was used to prepare hand scattered prepregs and to remove moisture of prepregs. Heating capacity is maximum 250C.

3.2.5 Hot press

Carver 3856CE Model laboratory type hot press was used for composite part manufacturing out of prepregs by compression molding. Press has a maximum 22 ton pressure, 300°C temperature capacity (Figure 3.8).

Figure 3.8 : Hot press for compression molding.

3.2.6 Metal molds

The molds used for compression molding is stainless steel. Dimensions of the molds are 250 mm X 250 mm with a thickness varying as 3 mm, 6 mm and 10 mm.

3.2.7 Infusion system

Vinyl ester matrix composites were produced by means of sealed vacuum film on a glass surface via application of vacuum by a vacuum pump with 1 bar pressure capacity. A vacuum film with 250°C heat resisance was used to produce ISPCBP composites out of CBT prerpegs.

3.2.8 Mechanical test device 100 kN

Tensile, flexural and compression analyses were performed on Zwick Z100 model universal test machine with load cell of 100kN. Tensile grips have 100 kN capacity. A micro-extensometer was used for displacement measurement.

3.2.9 Mechanical test device 2 kN

The bond strength of the skin to the core material of sandwichs was measured by using Zwick Z2 model universal test machine with 2 kN of load cell.

3.2.10 Impact test equipment

Charpy impact test machine (Ceast Resil Impactor) was used to determine toughness of the composites. The apparatus consists of a pendulum axe swinging toward the v-notch in the test specimen.

3.2.11 Microscopes

Scanning electron and optical microscopy were performed on the peeled surface of the composites in order to investigate the effect of sizing on the interface bonding. Also the effects of process conditions on consolidation quality, void formation and fiber orientation were investigated. For this purpose Philips XL 30SFEG model SEM and Leica APO8 Model stereo microscope were used.

3.2.12 Furnace

Protherm PLF 110/10 model furnace has maximum working temperature of 1100°C. The furnace was used to determine fiber volume fraction of composites.

3.2.13 DSC

Differential scanning calorimeter (DSC) was performed on IPCBT-NCGF with DSC 6200 device, (SII NanoTechnology EXSTAR).

3.3 Production Methods

3.3.1 Production of IPCBT matrix composites

3.3.1.1 Preparation of pre-pregs with CBT powder

CBT prepregs are classified in two categories according to their preparation technique as hand scattered and machine scattered. Hand scattered pre-pregs were prepared with hand scattering method dispersing powder on weighing machine (Fig. 3.9). After scattering of powder onto the glass reinforcement, the pre-pregs were heated and the powder was melted at a temperature, which is higher than CBT's melting point, in drying oven. Prepreg was kept in the oven for 30 seconds after oven reached to target temperature (Figure 3.10). Thermopapers were used to see the temperature which prepreg surface reached (See Figure 3.11).

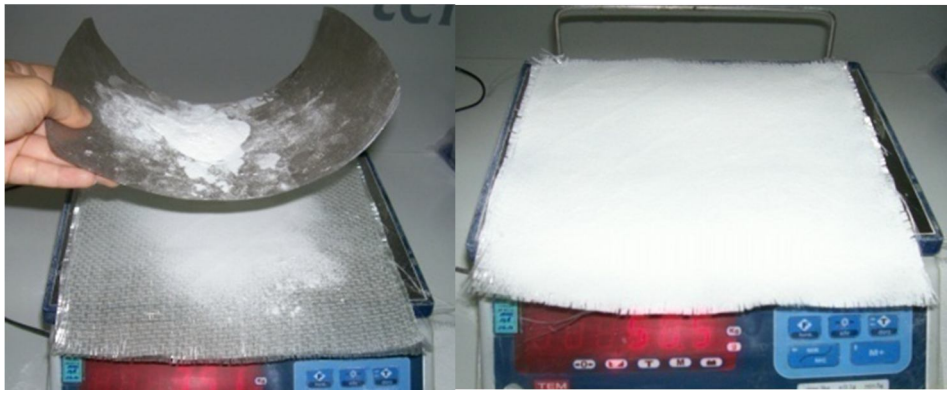


Figure 3.9 : Scattering of CBT powder on reinforcement on weighing machine.

Figure 3.10 : Pre-pregs kept in oven.

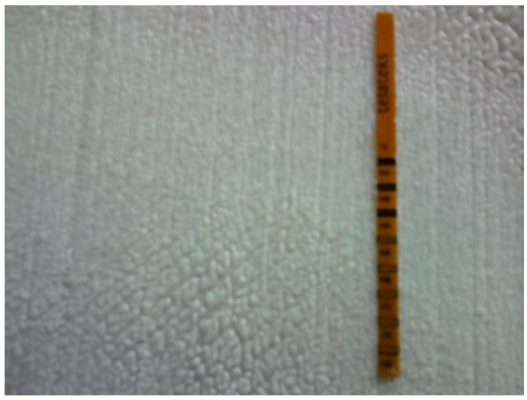


Figure 3.11 : Thermo paper placed on prepreg (after applied heat).

Machine scattered pre-pregs were prepared via scattering system using a scatter roller to sprinkle loose, coarser powder with a typical particle size of 0-500 micron or 200-300 micron, which is then firmly fixed on the substrate in an infra-red field as seen Figure 3.12. The thermoplastic powder is drawn from a powder funnel by a sprinkle roller. The powder is brushed out of this roller, falls through an oscillating sieve onto the base material. Subsequently the powdered material is fed through a sintering chamber. The adhesive is then heated with infra-red heaters and bonded to the base material and flattened by pressing rollers.

Fiber/Resin weight ratio was hold in a value of 70/30. This ratio was arranged with the speed of conveyor band of the system and the mechanic variator that provides controlling of scattered powder amount. Mechanic variator was hold in 1. Scattered reinforcement has been got through oven, which has a 2 meter distance, at suitable temperature determined in preliminary studies with hand-scattering method.

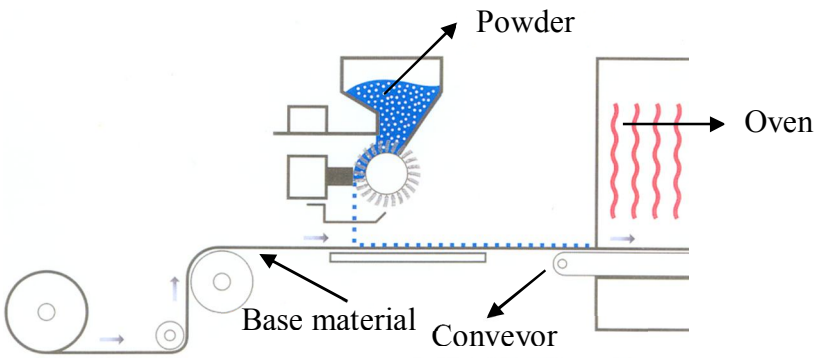


Figure 3.12 : Scattering system.

Temperature of the oven and the speed of conveyor band were arranged to achieve holding the substrate at 160°C for 15 sn application temperature and time. Prepregs which have 70/30 fiber/resion weight ratio successfully achieved, See Figure 3.13.

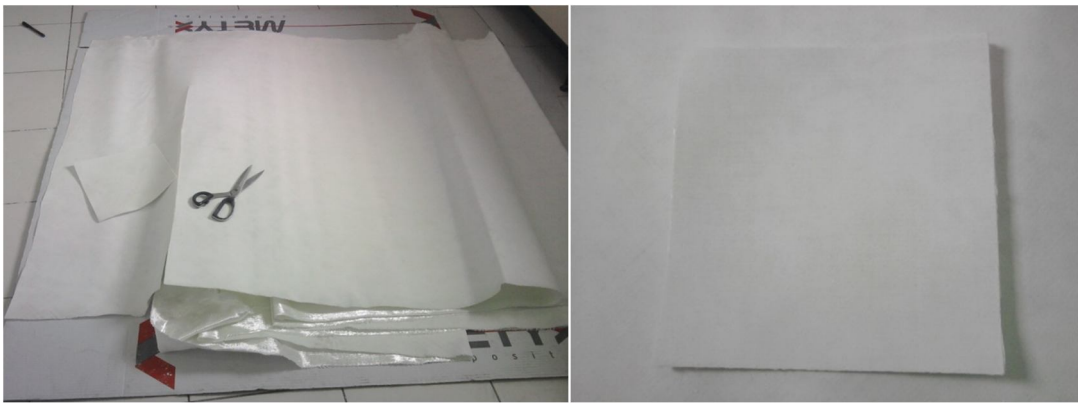


Figure 3.13 : CBT Prepreg: CBT coated X468 (left: whole fabric, right:cutted fabric).

3.3.1.2 Conditioning methods of pre-pregs before composite production

Before hot pressing process, pre-pregs were conditioned in an oven at 80°C for 12 hours to remove moisture on fibers and resin. Too see the moisture removing effect on composite laminates two kinds of wait time were compared after conditioning.

In first method the prepregs were processed in hot press as soon as they were taken off from the oven. In second method prepregs were subjected to heating at 80°C for 12 hours in the oven. Vacuum bagging was applied to take off the air from pre-pregs as soon as they were removed from the oven (See Figure 3.14).

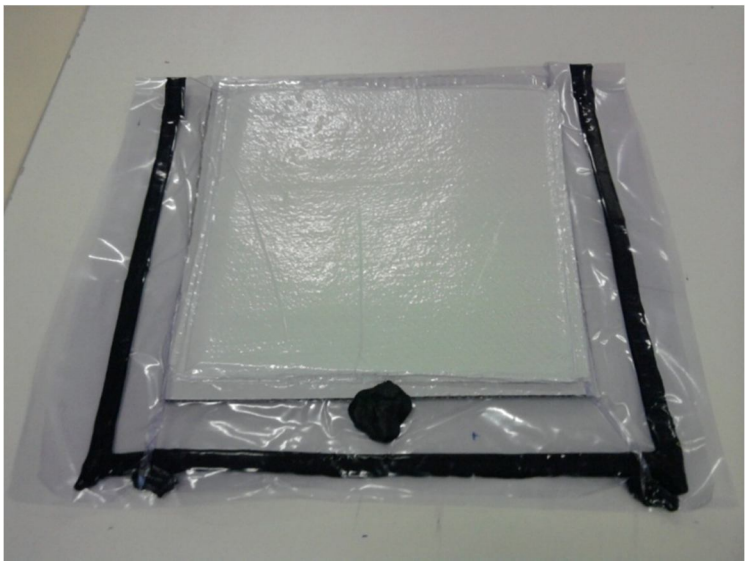


Figure 3.14 : Vacuum bagged prepregs.

3.3.1.3 Production of IPCBT composites in hot press

The number of the layers needed was calculated by formulation 3.1.

(Fiber density X Fiber ratio) + (Resin density X Resin ratio) = Composite density
Composite density X Mold depth= Total composite weight /m²
Total composite weight /m² X Fiber ratio = Fiber amount to use
Fiber amount to use/ Fiber weight per m² = Number of layers **(3.1)**

Table 3.1 presents the laminates weights and calculated thiskness values of the laminates according to fiber areal weights by using formulation 3.1. This table can be used for 70/30 fiber resin ratio. The calculated number of layers from the information above is given Table 3.2 for different fiber reinforcements and mold depth used in this study for 70/30 fiber/resin weight ratio.

The composites were produced using number of layers mentioned in Table 3.2. Beforethe prepregs were placed into the mold, all surface of the metal mold was coated with semi permanent mold release agent to achieve easy demolding preventing sticking the part on mold surface. Pre-pregs were placed into the mold as in Figure 3.15. It was covered with a heated metal plate and placed to center of the pre heated hot press to desired temperature, See Figure 3.16.

Table 3.1 : Calculated thickness chart according to fiber weights.

	Fiber areal weights for several layers, g/m^2					
Fabric areal weights	5 layers	10 layers	15 layers	3 layers	6 layers	9 layers
450	2250	4500	6750	1350	2700	4050
600	3000	6000	9000	1800	3600	5400
850	4250	8500	12750	2550	5100	7650
	Laminate areal weights for several layers, g/m^2					
Fabric areal weights	5 layers	10 layers	15 layers	3 layers	6 layers	9 layers
450	3000	6000	9000	1800	3600	5400
600	4000	8000	12000	2400	4800	7200
850	5667	11333	17000	3400	6800	10200
	Calculated Thickness, mm					
Fabric areal weights	5 layers	10 layers	15 layers	3 layers	6 layers	9 layers
450	1.8	3.6	5.4	1.1	2.1	3.2
600	2.4	4.8	7.2	1.4	2.9	4.3
850	3.4	6.8	10.1	2.0	4.1	6.1

Table 3.2 : Number of layers for prepregs with 70/30 fiber resin ratio.

Reinforcement Code	Mold depth, mm	Number of layers, pcs
X600	3	6
X600	6	12
X600	10	20
X468	3	8
X468	6	16
X468	10	26
L600	3	12

Figure 3.15 : Prepregs in metal mold.

Figure 3.16: Metal mold in hot press.

A constant pressure was applied to hot press for desired period. After the time was completed metal mold was removed from press to demold the part. Sucessful composite plates were achieved after demolding, See Figure 3.17.

Figure 3.17 : IPCBT composite flat plate with 3 mm thickness.

3.3.1.4 Production of IPCBT composites by vacuum consolidation

5 layers of CBT prepregs consisting of X600 were vacuumed with the vacuum film by vacuum pump on a heatable metal plate. The plate was subjected to heating at 200°C for 1.5 hours. After the time was completed the plate was removed from oven and left to cool at ambient temperature.

3.3.2 Production of PBT matrix composites from commingled fabric

TPX750 coded Glass/PBT commingled fabric was produced using hybrid yarn commingled in air jet texturing system. +45°/-45° non crimp fabric has the same structure as X600. 8 layers of TPX750 were placed into hot press. Placement of the fabic layers was done between two teflon films into heating plates, which has 200°C temperature, for easy demolding. Then the press was heated to 260°C. Compression runs at 260°C with a constant pressure of 1.5 MPa for 30 minutes. Press was cooled to 200°C before removing of composite plate after 30 minutes compression time was completed. The part was left to cool at ambient temperature.

3.3.3 Production of PA matrix composites

Firstly the glass fabric (X600) was dipped into CoPA suspension in the fluard bath. Excess of the liquid was removed by squeezing with the rollers. Pressure of the rollers was hold in 4 bar, and speed of rollers was 5.5 rpm, See Fig. 3.18 and 3.19

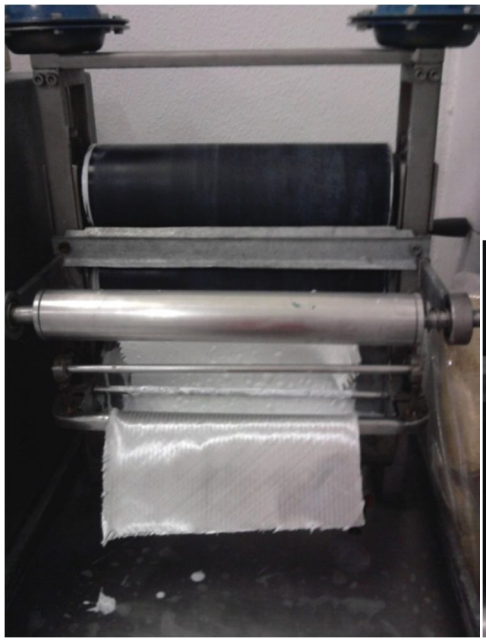


Figure 3.18: Fluard bath.

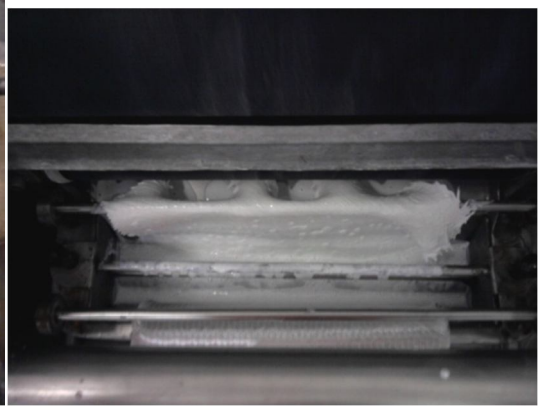


Figure 3.19. Squeezing of the excess liquid through the rollers.

After impregnation of the glass fabric with suspension, the wet fabric was placed into the oven to leave it for drying. 130°C, 2 minutes was enough for evaporation of the water and drying (Fig. 3.20).

Figure 3.20: Wet fabric placed in oven to dry.

Dry fabric was weighed to analyse resin content in the fabric. For 4 bar roller pressure was achieved % 7.6 resin weight ratio. To increase CoPA content roller pressure was decreased to 1 bar. The resin content which is 7.58 % with 4 bar roller pressure was increased up to 10.9 % with 1 bar roller pressure.

Dried impregnated fabrics with CoPA were cutted to the dimensions of 25 cm X 25 cm. PA12 powder was scattered by hand onto impregnated fabric on weighing machine to catch 70/30 fiber/resin weight ratio for both X600 and X468 coded multiaxials (Fig. 3.21). Here, total resin content of CoPa and PA 12 were hold as 30% weight ratio. After scattering the fabric was placed into oven to melt and fix PA12 to the fabric at 190°C for 3 minutes (Fig. 3.22).

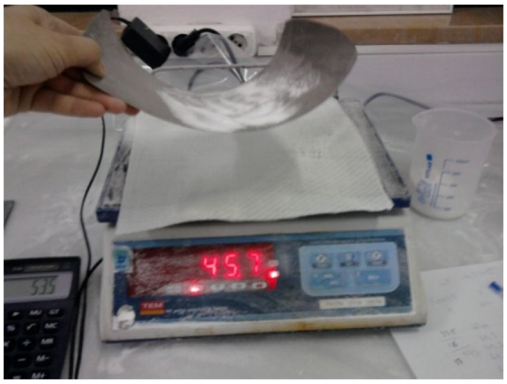


Figure 3.21: Scattering of PA12 on fabric impregnated with CoPA .

Figure 3.22: PA12 scattered fabric placed in oven for melting and fixing of the polymer.

6 layers of pre-pregs were placed into 3 mm metal mold (Fig. 3.23). Hot press temperature was hold at 200°C and 210°C for 15-20 minutes with a 22 ton pressure (See Figure 3.16). As soon as compression period was completed, the metal mold removed from press. The part was left to cool at ambient temperature in the mold.

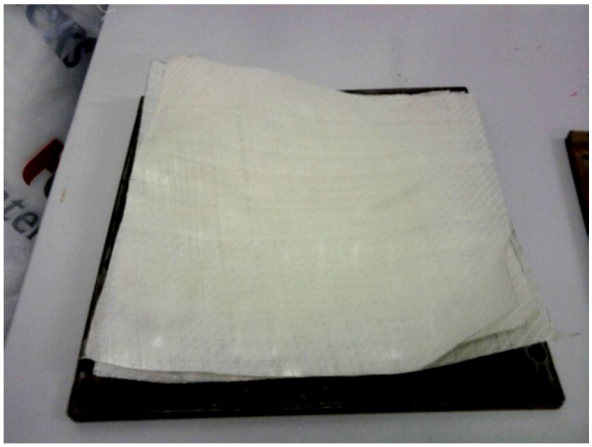


Figure 3.23 : Glass fiber pre-preg placement into the mold.

3.3.4 Production of VE matrix composites

VE composite laminates having 8 layers of L300 were manufactured via vacuum assisted resin transfer molding process. 2% cumyl hydroperoxide was mixed with the resin prior to impregnation as curing agent. Vacuum bagging was done at the room temperature and under 0.9 bar pressure applied by means of vacuum pump. Cured parts were subjected to post curing at 80˚C for 3 hours.

3.4 Characterization Methods

3.4.1 Fiber ratio and void content analysis

The fiber volume fractions (V_f) of the composite panels were determined using the matrix burn out method. In this method, composite laminates were burned in a high temperature furnace at about 600°C. The remaining fibers were weighed and the volume of the fibers was calculated based on the mass and the density of the fibers and the matrix. The void content of the samples was determined by carrying out density measurements according to ASTM D2734, followed by burn-out tests.

3.4.2 Mechanical characterization

At least five specimens were tested for each test case for the derivation of average test values. Since direct comparisons may not be valid if test specimens with different fiber volume contents are tested, mechanical analysis results were normalized according to fiber volume fraction for a good comparison. Normalization is a procedure for adjusting raw test values to single (specified) fiber volume content.

Since fiber-dominated strength and stiffness properties vary linearly with fiber volume fraction, an obvious first approach would be to determine the actual fiber volume fractions of the test specimens by an appropriate method and to adjust raw data values by the ratio of a common fiber volume fraction (chosen or specified) to the actuals as shown in Equation 3.2 [60].

$$\text{Normalized value} = \text{Test Value X} \frac{V_{fnormalizing}}{V_{fspecimen}} \quad \textbf{(3.2)}$$

Where $V_{fnormalizing}$ is the chosen fiber content (volume fraction or %) and $V_{fspecimen}$ is the actual fiber content (volume fraction or %). All analysis results were normalized to 55% volume fraction because this ratio is the closest value to average one.

3.4.2.1 Tensile analysis

Tensile tests of composite specimens were performed as described in ASTM D3039 test standard. Test specimens were subjected to uniaxial tension with a constant displacement rate of 5 mm/min and corresponding stress-strain values were recorded for maximum tensile strength and elastic modulus determination both in transverse and longitudinal directions with respect to fiber orientation. A micro-extensometer was used for displacement measurement. Tensile analysis was also performed to determine bond strength between skin and core material in sandwich laminates.

3.4.2.2 Flexural analysis

Flexural strength and modulus of the laminates were determined via 3-point bending tests done according to ASTM D790. Span to depth ratio was hold as 16:1.

3.4.2.3 Compression analysis

ASTM D695 test standard was considered for compression tests. Constant displacement rate was set to 1.3 mm/min. Compressive strength and modulus of the laminates were recorded.

3.4.2.4 Impact analysis

The impact resistance of the composite specimens was determined via Charpy impact tests done according to EN ISO 179-2 test standard. Test specimens were notched as being 2 mm notch size according to the standard.

3.4.3 Optical analysis

Scanning electron microscopy was used for the cross sectional area and surface characterization aiming to show the fiber wetting, compatibility of the resin and micro void formation. Sputter deposition of thin conductive gold coating was applied onto the sample surfaces.

Stereo microscope was used for crossectional area analysis and determination of macro void and defects formation in composites.

3.4.4 DSC analysis

Differential scanning calorimeter (DSC) was performed on IPCBT composites. Analysis was carried out with 14 mg sample under nitrogen to prevent moisture and oxidative degradation. The heating and cooling rates were hold as 5 °C/min. Melting temperature (Tm) was taken as the maximum of the endothermic melting peak from

the heating scans, whereas the crystallization temperature (Tc) was considered to be the maximum of the exothermic peak of crystallization from the cooling scans.

The crystallinity ratios were calculated from the determination of the melting enthalpy of the samples. The degree of crystallinity was then defined as follows (Equation 3.3):

$$\chi_c(\mathrm{wt\%}) = \frac{\Delta H_m}{\Delta H_\infty} \quad \textbf{(3.3)}$$

where ΔHm is the area under the melting peak of the polymer, and $\Delta H\infty$ is the melting enthalpy of the fully perfect crystal of PBT. $\Delta H\infty$ was accepted as 142 J/g according to the literature [17].

4. RESULTS AND DISCUSSION

In this study, firstly prepregs were prepared and the composites were produced from these prepregs. For this purpose, CBT, PA and PBT matrix prepregs were produced using X600, X468, L300 and TPX750 coded fabrics. In order to identify optimum conditions of CBT prepreg production, X600 coded fabric and CBT matrix were used. Table 4.1 summarizes the process conditions of prepregs produced by hand scattering in laboratory and scatter coating machine and composite production conditions by compression molding.

Table 4.1 : Prepreg and composite production conditions.

Prepreg Production			**Composite Production**		
Method	**Temperature, °C**	**Time, s**	**Temperature, °C**	**Time, min.**	**Pressure, MPa**
Hand Scattering	160	30	200	30	1.6
Hand Scattering	155	30	200	30	1.6
Hand Scattering	180	30	200	30	1.6
Scatter Machine	145	10	200	30	1.6
Scatter Machine	155	15	200	30	1.6
Scatter Machine	160	20	200	30	1.6

According to the mechanical test results of these composites, it was concluded that the most proper temperature for both hand scattering and machine scattering system is 160°C. Twenty seven kinds of composite were prepared from five kinds of X600-CBT prepregs by using these optimized conditions. During the composite production from these prepregs different compression molding parameters such as temperature, pressure, time, different processing cycles and vacuum bagging method were tried. Considering the thickness and fiber volume fractions of the composites, the effects of the production parameters and methods on composite properties were evaluated by mechanical and optical analyses. In the optimization trials of compression molding temperature, pressure, and time, two parameters were held constant when one parameter was tried. Composite samples with 55% volume fraction were produced using five different pressures between 0.9-2.8 MPa, three

temperatures between 190-210°C, five different time periods between 10-30 minutes. In order to investigate the influence of demolding temperature on composite properties, three kinds of composite were produced at 200°C, 1.6 MPa, 30 minutes compression conditions demoulding at different temperatures such as 200°C, 180°C, 160°C. Moreover, five composites with different V_f values between 55-65% were produced at 200°C with 1.6 MPa pressure for 30 minutes and investigated. The composites with different thicknesses as 3, 6, 10 mm were produced at 200°C and 1.6 MPa for 30 minutes. The effects of pre-impregnation time on composite properties during compression molding were investigated with the trials of different process cycles. For this purpose, four different composites were prepared at 160°C and 170°C pre-impregnation temperatures and 5 and 10 minutes pre-impregnation periods. The prepregs of composites mentioned above were kept in the oven for 12 h at 80°C. Some prepregs were subjected to four different kinds of conditioning. The composites of these prepregs were produced at 200°C and 1.6 MPa for 30 minutes and the conditioning effects on composite properties were investigated by mechanical and optical analysis.

PA matrix prepregs were prepared with the method mentioned in Section 3.3.3 different than that of CBT prepregs. Two kinds of PA prepreg with X600 were used to produce four kinds of composites at temperatures between 200-210°C with 3.0 MPa for 15-30 minutes.

Two kinds of prepreg including X468 and CBT with 55% V_f were produced using the optimization conditions achieved from the trials of X600-CBT with hand scattering and scatter coating mechine methods. Two composites with 3 mm thickness were produced from these prepregs at 200°C, with 1.6 MPa pressure for 30 minutes after the prepreg was conditioned at 80 °C for 12 hours. Demolding temperature was 200°C for both composites. One PA matrix prepreg including X468 with 50% V_f was produced as mentioned in Section 3.3.3, and then it was subjected to compression molding to achieve 3 mm thickness composite at 210°C with 3.0 MPa pressure for 20 minutes.

One kind of prepreg with 54% V_f was prepared with L300 code fabric and CBT to produce UD and ±45° composites. Moreover, VE matrix composites including L300 were produced by vacuum infusion method without preparing prepregs. VE matrix composites in 3 mm thickness were prepared at ambient temperature and 1 atm pressure for 24 hours.

For comparison of conventional PBT and IPCBT, the composite with conventional PBT matrix was produced using TPX750 coded prepreg including commingled glass fibers and PBT fibers supplied from Metyx Composites®. Composite production was carried out by compression molding at 260°C, with 1.5 MPa pressure for 30 minutes demolding at 200°C.

Sandwich structure composites from CBT prepregs and PA prepregs were done using PA foam as core material by compression molding. Two kinds of X600-CBT skin sandwich were produced using two different process conditions in compression molding. One kind of X600-PA skin sandwich was produced by compression molding.

4.1 Optimisation of Production Conditions of CBT Prepregs

Since CBT is polymerised in situ, the processing method of IPCBT is different significantly from conventional thermoplastic processing. It is mentioned in previous sections that the main reason of using reactive thermoplastic resins is the requirement of a complete impregnation to achieve good composite properties. The continuous and rapid increase in the viscosity during processing of CBT with in situ polymerisation, limits the time needed for the impregnation of fibers. Here, the impregnation time is defined as the time when the reactive polymer system reaches a viscosity of 1 Pa.s. Available impregnation time with low viscosity can change between 2-8 minutes depending on temperature and polymerisation catalyst [42, 43]. Although, the fiber bundles in the prepreg were pre-impregnated with CBT, still the inner fibers have to be wetted with the resin during composite production process. In order to hold available impregnation time as much as longer to ensure complete wetting of all fibers, the prepreg preparation temperature has to be lower than polymerisation temperature of CBT/catalyst mixing. CBT resin does not have an exact melting point since it consists of a mixture of oligomers, but it has a melting range which lies between 120 and 160°C and the polymerisation starts at 180°C. In order to see the influence of the pre-preg preparation temperature applied after scattering of CBT powder precombined with its catalyst, the different temperatures were tried. The trial temperatures were arranged in such a way that the temperature will be lower than 180°C, but will also allow for melting of CBT and sticking onto the glass fibers. The general production parameters have been discussed detailed in Section 3.3.1.

4.1.1 Laboratory scale trials

Laboratory oven adjusted to 160°C, 170°C and 180°C. Application time at the target temperature was chosen as 30 minutes. The composite parts were produced from these prepregs by compression molding in hot press as explained in Section 3.3.1.2 and subjected to the tensile and flexural tests to determine most appropriate prepreg production temperature. Hot press parameters are 200°C press temperature, 1.6 MPa pressure, 30 minutes compression time. The flat composite plates were produced with 3 mm thickness consisting 6 layers of X600 coded reinforcement. They were demolded as soon as 30 minutes hot pressing period was completed and allowed for cooling at ambient temperature in the mold. The tensile and flexural strength comparison can be seen in Figure A.1 (a). According to the results normalized to 55% volume fraction, it can be seen that 160°C oven temperature gave the highest tensile and flexural strength. Tensile and flexural modulus values showed the same tendency as well, Fig. A.1 (b). The significant decrease in strength and modulus with increasing prepreg production temperature like 180°C may be attributed that the polymerisation starts during prepreg production prior to compression process resulting a viscosity rise which can affect the impregnation of the resin.

4.1.2 Scatter coating machine trials

The hand scattering method was a laboratory scale prior study for prepreg production to identify optimum production parameters of the real scattering system. A crosscheck had to be done in the real scattering system using similar parameters used in hand scattering method comparing the end composite properties. For this purpose, the trial temperature and time of the real scattering system were arranged as the prepreg surface can reach up to 160°C. However, to reduce the process time for saving the time during real prepreg production, the temperature was increased and the process time was decreased in the production line. Here, the important point is to reach up to 160°C on coated surface of the pre-preg. Therefore, machine temperature was arranged to 160°C and 170°C separately and the time was changed. The scattered sample passed through the oven for 20 seconds and 15 seconds. The temperatures which the prepreg surface reached were measured by using thermopapers as described in Section 3.3.1. See the Table 4.2 for different machine and prepreg temperatures.

Table 4.2 : Prepreg production conditions in scatter coating machine.

Reached temperature on prepreg surface, °C	Temperature of the machine, °C	Time, s
160	170	20
150	160	15
145	160	10

Flat composite plates were manufactured using the prepregs produced with different temperature and time described in Table 4.1. Composites were subjected to tensile and flexural tests. Figure A.2 (a) represents tensile and flexural strength change with the prepreg production temperature. Figure A.2 (b) represents the tensile and flexural modulus change with the prepreg production temerature as well. It can be clearly seen that the highest prepreg temperature of 160°C which prepreg sample reached showed the highest tensile strength and there is significant decreasing in tensile strength of the samples produced at the temperature below 160°C. The temperatures 150°C and 145°C which prepreg sample reached gave fairly low tensile and flexural strength as well as modulus values.

4.1.3 Conditioning of prepregs before compression

In fact, it is well known that drying is important for proper polymerisation of the CBT resin into PBT. If the moisture content is too high, the material will not polymerise properly (See section 2.6.2). For this reason, to obtain maximum molecular weight build besides drying CBT resin, fibers/fillers, additives and molds should also be dried and free of moisture before polymerisation of CBT resin takes places. All the materials must be dried and maintained in a dry condition throughout the melting and polymerisation stages [61]. Taking into account this information, to avoid any risk of moisture the prepared prepregs were dried overnight at 80°C kept in an oven for the preliminary studies. In fact, if it is looked at the commercial side, drying process causes energy consumption and time loss. Therefore, in this section different conditioning methods were applied to save energy and time for commercial viability. Composite parts were produced using the prepregs conditioned with different methods and tensile tests were performed for comparison.

- In the oven method the pre-pregs were hold in the oven at 80°C for 12h and they were molded in hot-press by taking quickly from the oven to the mold to not allow for exposure air.

- In the vacuum bagging method, firstly pre-pregs were hold in oven at 80°C, 12h and they were quickly vacuumed by using a vacuum film by means of vacuum motor to take air. These prepregs were left to wait for 2 days in vacuum bag at ambient temperature. They were molded in hot press as soon as the vacuum film was removed.
- Another sample was conditioned with the same method of vacuum bagging. However, the prepregs were kept in the oven at 80°C for 10 minutes after vacuum bag was removed, then pressed in press taking from the oven.
- One composite sample was prepared with the prepregs which were not conditioned allowing for exposure to ambient temperature.

Table 4.3 presents the tensile properties of the composites produced from the prepregs which were conditioned with different methods. If we look at the tensile properties of the unconditioned sample, we can see that significantly lower strength and modulus values as compared to that of the sample conditioned in the oven clearly support the claim of removing moisture obtained from literature. It is clear that the vacuum bagging in both cases causes tensile strength and Young Modulus reducing more than 50%. A low tensile strength and modulus are, therefore, an indication of poor matrix properties because the proper polymerisation couldn't achieve. If we compare the properties of the unconditioned sample and vacuumed samples, their close strength values and remarkable modulus decreasing show that the vacuum bagging is not a kind of suitable method to remove moisture from the prepregs.

Table 4.3: Tensile properties of IPCBT composites conditioned with different methods.

Vf, %	Conditioning method	Max.Tensile Str, MPa	Modulus E, GPa	Max.Strain, %
53	No conditioning	163±11.8	16.7±1.4	3.5±0.8
51	Oven	394±11.3	20.8±0.8	2.1±0.1
50	Vacuum	159±4.6	13.5±0.3	1.8±0.1
50	Vacuum 10 min.@80°C	177 ±2.5	12.7±0.3	3.8±1.2

4.2 Optimisation of IPCBT Composites Production by Compression Molding

In this section, the effect of composite production conditions in compression molding on composite properties is clarified. For this purpose, + 45°/-45° biaxial X600-CBT prepregs were used for the manufacturing of composite test samples in hot press as described in section 3.3.1.2. The composites were characterised by tensile and impact tests. These tests were performed to determine the most suitable hot press parameters to achieve IPCBT composites with the proper mechanical properties.

All the mechanical analyses were done only on main fiber axis as if the longitudinal axis since the glass fiber reinforcement has balanced fiber distribution on two directions of +45° and -45°. The impregnation quality was investigated by SEM and stereo microscope. The determination of the overall void content was done as mentioned in Section 3.4.1.

4.2.1 Compression molding pressure

We assume that the application of pressure facilitates the flow of the low viscosity CBT to penetrate into the fiber bundles and ensuring the complete wetting of them. In order to clarify the effect of the pressing pressure on properties of CBT composites, 5 different pressures were applied varying from 0.9 to 2.8 MPa. In these trials, hot press temperature was hold at 200°C for 30 minutes. Demolding of the composite parts was done applying rapid cooling at ambient temperature described in Section 4.1.

Figure A.3 (a) demonstrates the effect of pressure on tensile and flexural strengths of IPCBT composites. It is clear that the composite produced with 0,9 MPa pressure gave the lowest strength values for both tensile and flexural showing a big difference in respect with the other composites produced with higher pressures. It can be seen that the tensile strength doesn't show a significant difference for pressures between 1.6-2.8 MPa. If flexural strengths are taken into account it can be seen that higher pressures than 1.6 MPa give lower strength values. Figure A.3 (b) shows tensile and flexural modulus varying with different pressures. 1.6 MPa pressure gave the highest tensile and flexural modulus values while other pressures do not show significant difference between modulus values.

The void content measurement gave a result of 10.12±2.0% for the sample produced with 0.9 MPa pressure. This decreasing may be attributed to the micro voids formation due to the poor impregnation with insufficient pressure.

4.2.2 Compression molding temperature

In order to identify the most appropriate compression temperature three trials were carried out at 190, 200 and 210°C temperatures. Compression time and pressure were hold as 30 minutes and 1.6 MPa respectively. Demolding of the composite parts was done applying rapid cooling at ambient temperature as described in section 4.2.1. Figure A.4(a) shows how to change of the tensile and impact strengths of IPCBT composites at different compression temperatures. It is clear that there is not considerable difference between the tensile strengths at different temperatures. However the impact strength of the IPCBT composite increased by the application of 200°C compression temperature. On the other hand, it is obvious that the pressing temperature affected tensile modulus of the composites. It can be seen that the composite produced at 200°C gave the highest tensile modulus showing a big difference in respect with the other composites produced at 190°C and 210°C, see Figure A.4 (b). Low impact resistance of the composites can be caused by poor fibre-matrix interface properties as well as brittle behaviour of the matrix. SEM images of the composites show that there is good fibre-matrix interface property and there are no much micro voids which can act as stress concentration sites and leads to premature failure of the composites, See Figure A.5 (a, b, c). Thermal characterization by DSC was done to the matrix of IPCBT composite produced at 200 C. Table 4.4 summarizes the melting temperatures and enthalpies associated with the first and second DSC heating, as well as the crystallization temperatures and crystallization enthalpies, deduced from the cooling regime. Fig. 4.1 shows typical DSC thermograms of IPCBT for the first and second heating at 5^{o}C/min from 0 to 260^{o}C. Crystallization degree (X_c) was calculated as 23.5% according to Equation 3.3 given in section 3.4.4.

Table 4.4 : Melting temperature and enthalpies of IPCBT composite.

	1st Melting	Crystallization	2nd Melting
$T_{m,\,I}$ (^{o}C)	-	193.2	215.8
$T_{m,\,II}$ (^{o}C)	223.7	-	223.7
ΔH (J/g)	45.7	33.4	31.2

The existence of the melting peak indicates that complete polymerization and crystallization processes have taken place. The double melting peak results from the melting and recrystallization of imperfect crystals [63]. The appearance of double melting peaks would therefore be an indication of poor crystal quality in the composite part related to the time window for crystallization.

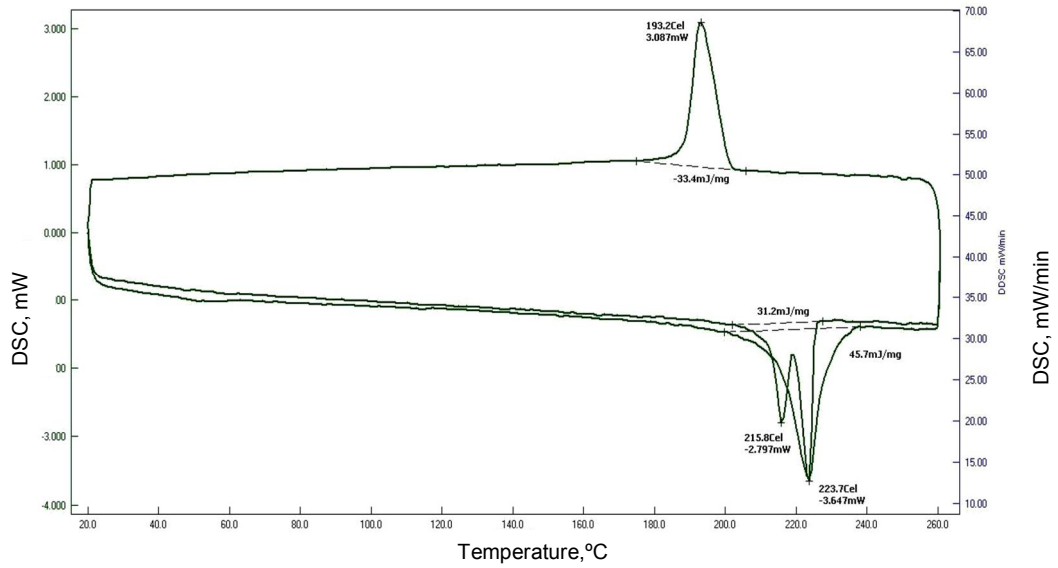


Figure 4.1 : DSC thermogram of IPCBT composite produced at 200°C.

If the polymerisation temperature is hold below the polymer melting point, and allowed sufficient time to cold crystallize at this temperature crystal quality can be increase [19]. However, high X_c is not desirable property for IPCBT composites since the high crystallinity decreases toughness correspondingly the impact strength.

In earlier studies it was recorded that when this resin is used under RTM-processing conditions, the matrix material is much more brittle than normal PBT [18]. This brittleness is induced by the isothermal RTM-production process, where rapid cooling is difficult [23, 56]. Brunelle et al. [52] indicated that polymers synthesized from cyclic oligomers displayed higher enthalpies of melting (60–80 J/g) hence, higher X_c as compared to the conventional PBT with enthalpies of melting ranging from 35–50 J/g. Therefore, toughening of IPCBT by adding comonomers is an aspect which is now under investigation [64].

Consequence, it can be said that achieved X_c as 23% which is lower than recorded values up today indicates that the compression molding of CBT prepregs is a suitable process to have composites with proper toughness and impact resisstance.

4.2.3 Compression molding time

It is already known from the prior studies that CBT can polymerise between 180-260°C. According to this information the trials were done to examine process time at 200°C compression temperature to carry out the trials in an isothermal way since this temperature is lower than expected melting temperature of the end polymer. Press pressure was hold stable at 1.6 MPa. After compression period was

completed, the composite part was removed from the press with the metal mold and left to cooling rapidly at ambient temperature. All parts were subjected to tensile and impact tests and compared with each other.

Figure A.6 (a) demonstrates tensile and impact strength variation of composites molded with different pressing periods varying from 10 to 30 minutes. The composite produced with 30 minutes gave the highest tensile and impact strength values. Although, there is not significant differences between tensile strengths of the composites produced with 20, 25, 30 minutes, the Young Modulus value of the composite molded for 30 minutes is quite high than those of the others, see Figure A.6 (b).

The longest pressing time resulted in a significant enhancement of both stiffness and strength. These differences in stiffness may be attributed to the higher molecular weight or higher crystallinity degree of the matrix.

It is clear that the sufficient tensile strength and impact resistance values can be achieved with 25 and 20 minutes when they were compared with 30 minutes. The composites pressed with the pressing time lower than 20 minutes showed big decreasing in tensile and impact properties. This result shows that the pressing time below 20 minutes is not sufficient to produce composites from CBT prepregs. This significant decreasing may be attributed to the uncompleted polymerisation in an insufficient polymerisation time resulting low molecular weight and oligomer impurity in the matrix.

The quality of the CBT impregnation was investigated by polishing the cross-section area of the composites and viewed under SEM. Figure A.7(a, b, c) shows cross-sectional area images of the composites for different pressing time. It can be seen that the image of composite produced in 10 minutes has a damaged and rough surface appearance. This rough looking of the matrix and broken fibers indicate the weak matrix property due to probably uncompleted polymerisation. However SEM images reveal that the composite laminates have well-impregnated area with only a few micro voids resulting in an overall void content of 3.7±0.9% according to burn out tests. Micro voids formation probably caused by the trapped air during the hot press moulding. However, any macro void which is possible to be formed between the glass bundles was not observed in the cross section of IPCBT composites.

The results reveal that a good impregnation was achieved in IPCBT composites in fact. Furthermore, the void content value obtained in this study is within the range of void content reported by other workers for noncrimp glass fabric composites. Parton

[19] quoted void content value of 4.2±1.7% and large inter bundle voids for UD IPCBT composites with 0.54 of V_f produced by RTM method. Another study by Vendramini et al. [13] reported a void content value as 3% for UD glass fiber reinforced PBT composites with 0.50 of V_f produced from commingled PBT/Glass fiber by hot compression at 240°C under pressure.

When the SEM images and void content calculations were compared with the reported data of different production methods of PBT composites it can be said that the pre-impregnation of fibers with CBT named as prepreg can improve wetting ability and eliminate the big void formations.

Figure A.8 represents SEM micrograph of the peeled out surface of IPCBT composite. The Image confirms that there is a good interfacial bonding between the fiber and resin, IPCBT matrix strongly adhered to the fiber surfaces.

4.2.4 Demolding temperature: Rapid and slow cooling

Isothermal processing is an obvious advantage for the composite production in hot compression process, see Section 2.6.2. Since the melting and molding temperature of the resin are both the same, isothermal processing is possible for CBT resin. This means that both polymerisation and crystallisation take place at the same temperature. However, to allow the part for cooling at ambient temperature after demolding at 200°C can be assumed as a rapid cooling. If the part is cooled down slower in the mold before demolding, this allows for crystallisation of the matrix.

It is well known that the crystallisation degree of the matrix can affect the mechanical properties of the composites significantly. Therefore, to observe the influence of demolding temperature on mechanical properties, 3 composite parts were produced at different demolding temperatures. After hot-press period was completed at 200°C, the press was cooled slowly to demolding temperature which is aimed to reach. The composite part was removed from the press at demolding temperature and allowed for cooling at ambient temperature in the metal mold.

The mechanical properties of the parts demolded at different temperatures were compared with those of the composite part demolded at 200°C. Compression conditions of the composites were hold as 200°C, 1.6 MPa, 30 minutes for all samples. Different cooling rates can be observed on temperature-time curve of cooled laminates after compression, see Figure 4.2.

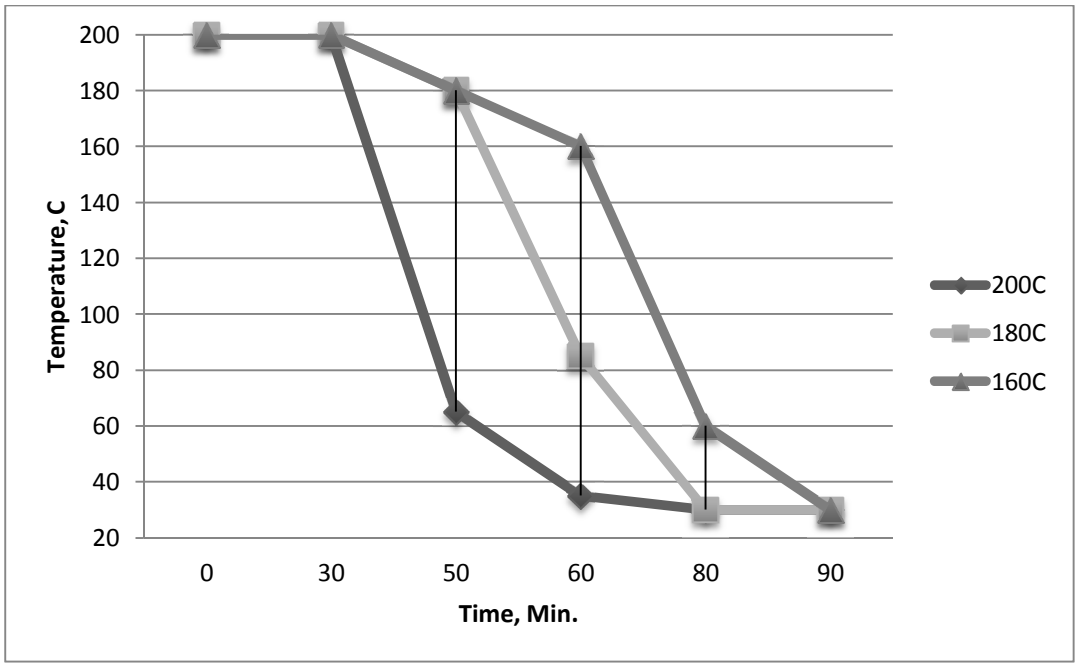


Figure 4.2 : Cooling speed after compression: Temperature-Time curve.

Figure A.9 (a) shows the tensile and flexural strengths of IPCBT composites demolded at different temperatures. The flexural strength of 701 MPa and tensile strength of 504 MPa recorded for the part demolded at 180°C were quite high values considering strengths of the part demolded at 200°C, 546 MPa for flexural, 424 MPa for tensile strength. Although the tensile and flexural strengths of the part demolded at 160 °C are lower than those of the 180°C demolding temperature, but 160°C demolding temperature still have quite higher values than those of 200°C.

If tensile and flexural modulus values (Figure A.9 (b)) are compared each other, it can be seen that while felxural modulus of 180°C is higher than those of the others, there is no considerable difference between the tensile modulus.

From microstructural point of view, there are some possible reasons for this improvement. Apart from the presence of defects and micro voids high degree of crystallinity can substantially increase the strength of a polymeric material.

Moreover, if the impact properties of the same laminates are observed, it is clear that the composite part demolded at 200°C has the highest impact resistance (See Table 4.5). The lower impact values of slow cooled parts as compared to that of rapid cooled part clearly support the idea indicating that the slow cooling can increase the crystallinity degree of IPCBT matrix.

Table 4.5 : Impact strengths of IPCBT composites at different molding temperatures.

V_f, %	Demolding Temperature, C	Impact strength, kJ/m^2
52	200	191.94±8.1
53	180	160.14±10.5
52	160	148.01±5.8

4.3 Development of TP Composites: Various Matrices, Reinforcing Materials and Production Methods

4.3.1 Production methods

4.3.1.1 Production of IPCBT composites with different processing cycle

For reactive processing of thermoplastics, the processing time is very important. An important aspect of the composite producing process is to ensure that the all fibers are impregnated by the resin completely before the propagation step of the polymerisation, which involves a rapid viscosity rise, starts.

Rheological properties of CBT have been discussed in more detailed in Section 2.6.3. According to the data it is clear that at the polymerisation temperature of CBT although the initial viscosity is very low, the reaction, and hence the viscosity rise, proceeds rapidly. Reaching to the high viscosities in short time causes to decrease in the time for impregnation (time to reach 1 Pa s).

In this section, in the beginning of compression process the prepregs were hold for a specific time at the temperatures below CBT's polymerisation temperature to achieve completely impregnation before polymerisation starts. For this purpose, several composite parts were produced with X600 prepregs.

The beginning temperatures were choose as 160°C and 170°C taking into account this melting range which the polymerisation does not occur yet. The pre-impregnation times were hold as 5 minutes and then temperature was increasedup to 200°C and hold for 30 minutes. The press load was kept stable in 1.6 MPa during whole process. Temperature and time variation curves describing processing routes of the compression with pre-impregnation are depicted in Figure 4.3 and 4.4.

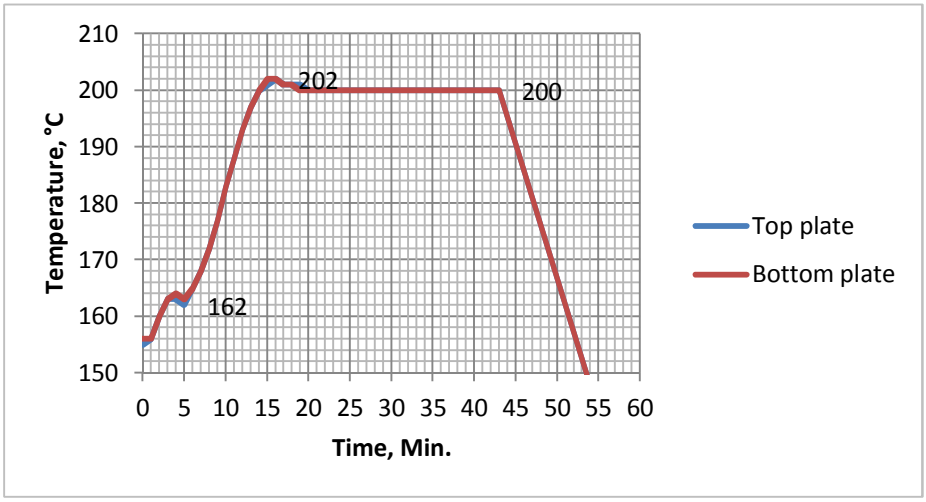


Figure 4.3 : Temp.-Time curve of compression for 160°C impregnation temp.

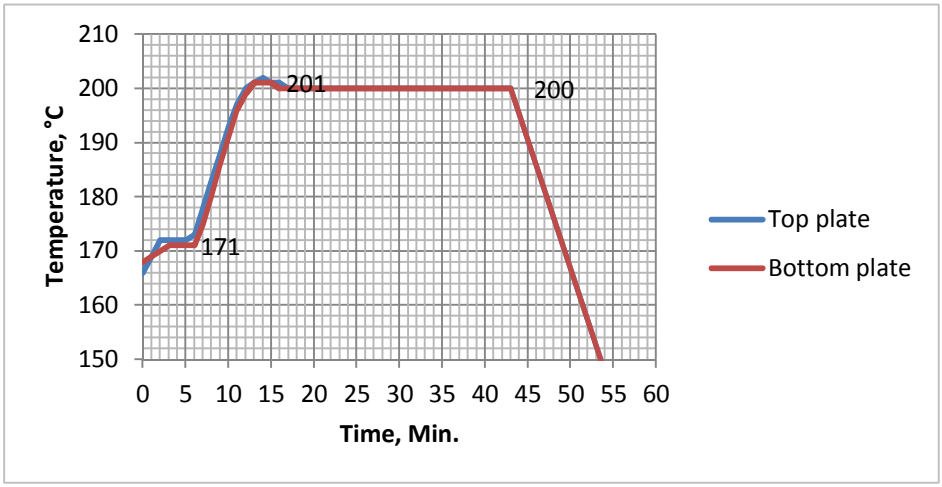


Figure 4.4 : Temp.-Time curve of compression for 170°C impregnation temp.

In order to assess the mechanical properties of the IPCBT composites produced with pre-impregnation route, tensile and flexural tests were performed and the properties of these composites were compared with those of the samples produced with the isothermal process at 200°C for 30 minutes. Comparison of the tensile and flexural strengths is shown in Figure A.10 (a). Tensile and flexural modulus values of different processing routes for 160, 170 and 200°C impregnation temperatures can be seen in Figure A.10 (b) as well. From the results presented in figures, it can be seen that composite produced without pre-impregnation has higher tensile strength and tensile modulus. It is clear that the influence of the pre-impregnation on the longitudinal tensile strength and modulus doesn't improve the tensile properties of IPCBT composites. The flexural strength on the other hand is affected more by the pre-impregnation route. Since the matrix strength dominates the transverse strength, good matrix properties can increase the transverse strength significantly

(10%). Increasing in flexural strengths with pre-impregnation application indicates that this route improve the matrix properties effecting the impregnation of fibers. However, higher modulus values both flexural and tensile of the composite produced without pre-impregnation sign that the different temperature routes decreases the stiffness of the matrix. This result can be attributed to influence of pre-impregnation temperature on crystallinity of IPCBT. Stereo microscope images of the composites prepared with pre impregnation at 160 and 170°C are depicted in Figure A.11(a) and Figure A.11(b) respectively. Cross-sectional are images of these composites show that the impregnation quality is good. Same pre-impregnation route was performed by taking the pre-impregnation time 10 minutes, and compression time 20 minutes instead of 30. This route was applied with 160°C and 170°C pre-impregnation temperatures. Recorded tensile strengths were 283 MPa for 160°C and 104 MPa for 170°C. Tensile modulus values were 18 GPa and 19 GPa respectively. In the cross sectional area images taken by stereo microscope of the composites, the raw appearances of the matrix indicate that it couldn't complete its polymerisation, see Figure A.12 (a) and A.12 (b). Quite low tensile strength and modulus values support this assumption. On the other hand, 10 minutes pre-impregnation period caused macro voids in the composites which can be easily seen in the stereo microscope images. These voids are probably caused by the air bubbles formation in the matrix during resin flow period due to the prolonged flowing time. After solidification of the matrix, the trapped air formed like macro voids which decrease the tensile strength.

4.3.1.2 Production of IPCBT composites by vacuum consolidation

Compression molding is a process which is useful for the fast production cycles and high pressures can be applied. However, its high tooling expenses limit to produce large composite parts due to the necessity of large mold dimensions and high pressures. For the large composite part production vacuum molding is preferable option in composite industry. In order to identify if IPCBT composites can be produced in vacuum consolidation process, CBT-X600 prepregs produced in machine scattering (160°C, 12') were subjected to vacuum molding as described in Section 3.3.1.3. Mechanical properties of the composites were identified by tensile and flexural analyses. Table 4.6 summarizes the tensile and flexural properties of the laminates produced with different two process routes. Apart from the flexural modulus, it can be said that vacuum consolidation gives better properties both in tensile and flexural tests.

Table 4.6 : Comparison of tensile and flexural properties of IPCBT composites after different process routes.

Process route	Max. Tensile Strength, MPa	Tensile Modulus, GPa	Max. Flexural Strength, MPa	Flexural Modulus, GPa
Vacuum Cons.	308±12	22±1	542±14	17±1
Compression	287±7	22±1	484±16	22±1

Figure 4.5 and 4.6 represents typical load-elongation curves recorded in three point bending mode.

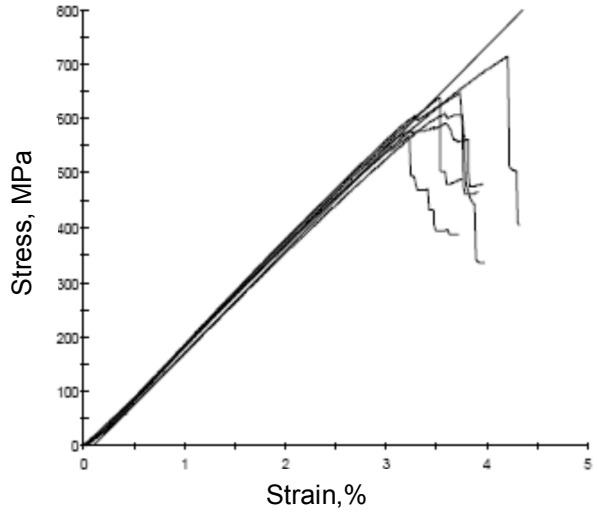


Figure 4.5 : Stress-Strain curve of IPCBT composites by vacuum consolidation.

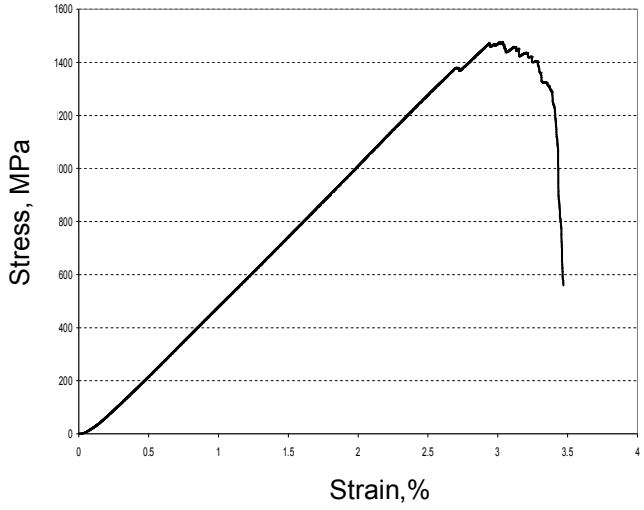


Figure 4.6 : Stress-Strain curve of IPCBT composites by compression.

Tendency of the characteristic flexural property curves indicates that IPCBT composites produced with compression and vacuum molding behave same.

4.3.2 Production of different structures of IPCBT composites

4.3.2.1 UD IPCBT composites and comparison with UD VE composites

To investigate mechanical properties of UD IPCBT composites, the pre-pregs were prepared using unidirectional glass fiber reinforcements (L300) as described in Section 3.1.1. Prepreg production was carried out using hand scattering method at temperature 160°C for 30 minutes. The fiber ratio of IPCBT composites were hold as 70% (w/w) which gives approximately 54% (v/v) fiber volume fraction (V_f). For the composite production from UD prepregs, the hot press conditions which have given best mechanical properties in preliminary studies were used. All composites were produced at 200°C pressing temperature with 1.6 MPa pressure for 30 minutes demolding at 180°C. The composites which include 12 layers of L300 reinforcements were subjected to tensile, compression on transverse and longitudinal load directions. In addition, one sample was prepared as that it consists of 12 layers glass fibers on +45°/-45° directions and subjected to tensile test. In Section 2.3.3 it was mentioned detailed about the advantages and disadvantages of thermoset resins and their important role in composite applications. It is known that vinylester resin is the preferred one because of its advantages and the lower price. Therefore, in this section the composites produced with vinyl ester resin using the same reinforcement L300 were compared with IPCBT composites. Production method was described detailed in Section 3.2.7. The fiber ratio of VE composites were hold as 54% fiber volume fraction (V_f). Table 4.7 summarizes the mechanical test results done with IPCBT and VE laminates. As an overall view, the weakness of IPCBT-NCGF laminates when compared with VE-NCGF laminates was clearly visible.

Table 4.7 : Tensile and compressive properties of IPCBT and VE composites.

	Max. Tensile Strength (MPa)	**Tensile Modulus (GPa)**	**Max. Tensile Strain (%)**	**Max. Compressive Strength (MPa)**	**Compressive Modulus (GPa)**
$(0)_{12}$ IPCBT	760±12	30.3±1	2.9	220±13	25.7±1
$(90)_{12}$ IPCBT	21±1	7.8±0	1.1	62±4	7.1±4
$(+45°/-45°)_{6s}$ IPCBT	83±6	7.6±0	12.7	-	-
$(0)_8$ VE	917±16	44.9±1	2.0	300±22	25.4±1
$(90)_8$ VE	44±3	11.6±0	0.6	128±2	10.1±1
$(+45°/-45°)_{4s}$ VE	137±2	15.3±0	17.5	-	-

The main problem that was predominantly effective in the fracture of IPCBT based laminates was the severe and early matrix cracking. This problem was initially identified from the transverse tensile and compression tests where matrix phase was carrying the majority of the load. Besides, the significant strength difference under longitudinal tensile loading may again be attributed to the occurrence of severe matrix cracking which initiated the overall catastrophic fracture (See Figure 4.7 and. 4.8).

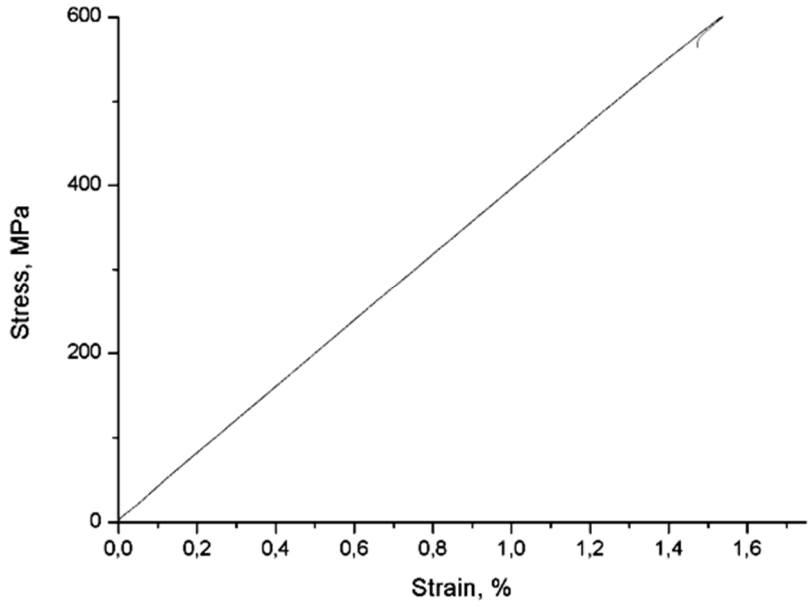


Figure 4.7 : Longitudinal tensile stress-strain curve of IPCBT composite.

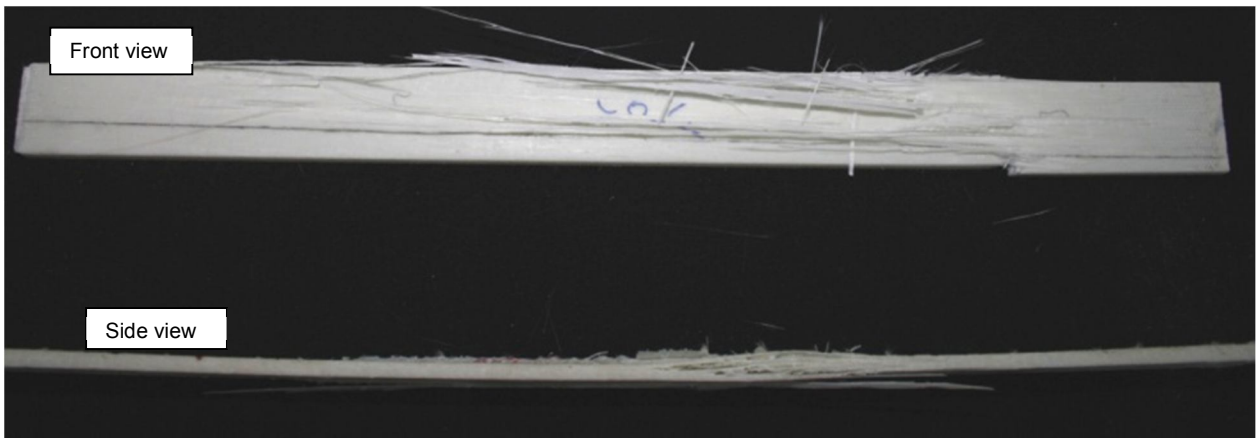


Figure 4.8 : Fractured IPCBT test specimens after tensile test.

In the compression analysis, the fracture mode of VE laminates was initial plastic fiber kinking followed by the final fiber fracture at the edge of the kink band, see Figure 4.9.

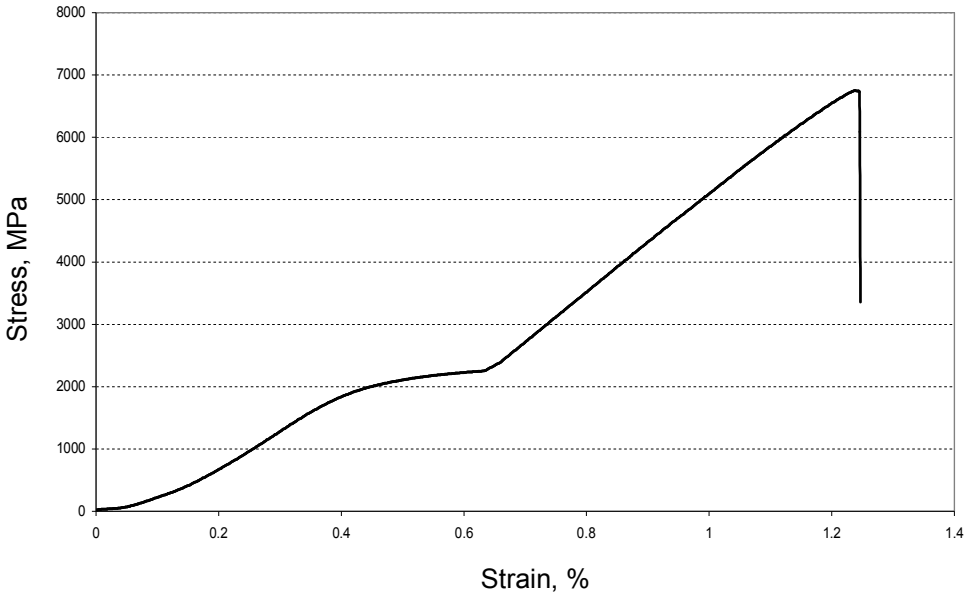


Figure 4.9 : Typical compression Stress-Strain curve of VE laminates.

The fracture of IPCBT laminates was either initiated by fiber kinking and followed by sudden delamination failure from the kinking crack tip or was directly caused by delamination, see Figure 4.10. Crossection images of test specimens before and after compression test supports delamination failure of IPCBT matrix assumption, See Figure 4.11.

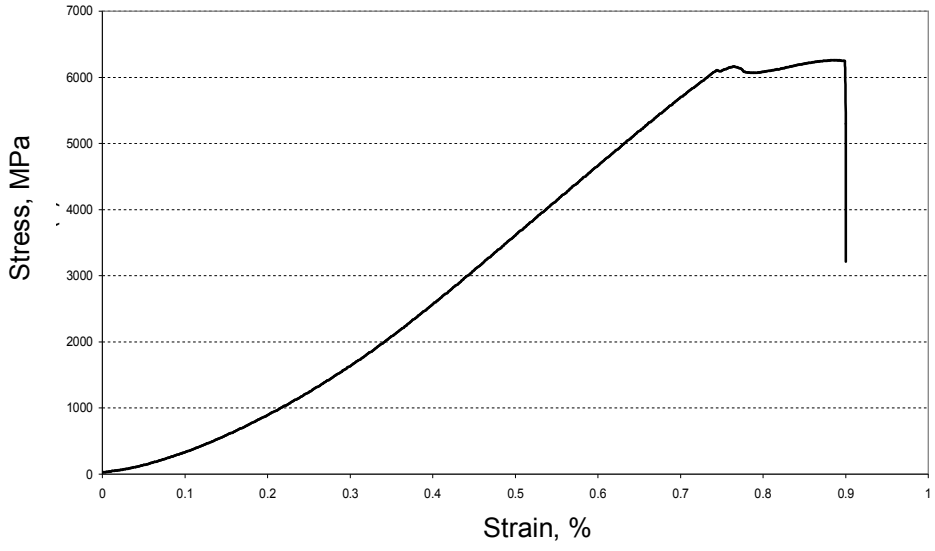


Figure 4.10 : Typical compression Stress-Strain curve of IPCBT laminates.

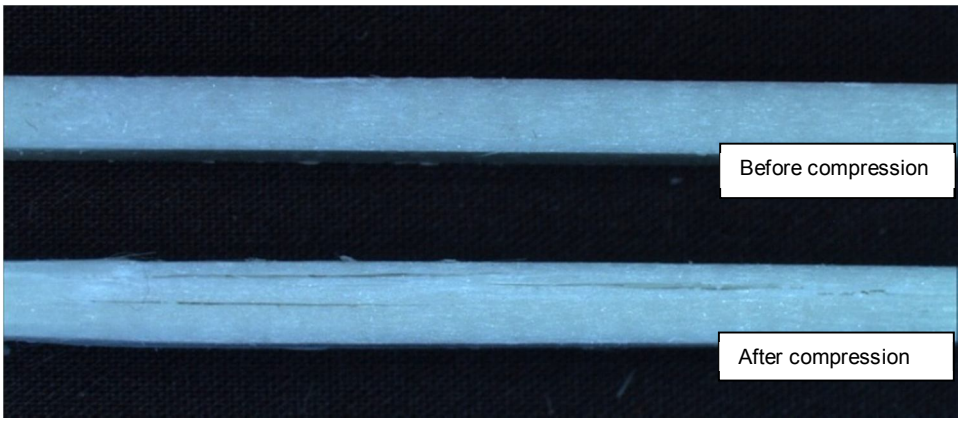


Figure 4.11 : Crossections of IPCBT test specimens before and after compression.

The main driving force in the occurrence of transverse matrix cracks may be attributed to the presence of uncontrolled residual stresses appeared during manufacturing process [65]. This behavior was initially identified from the testing of transverse tensile and compression tests where the matrix phase was carrying the majority of the applied load.

On the other hand longitudinal compression test results suggested a closer performance for both type of laminates. Correspondingly, the significant strength difference under longitudinal tensile loading was related with the initiation of transverse matrix cracks from critically stressed (residual+applied) regions. At this point it is vital to underline that the occurring of matrix cracks may be repaired for thermoplastic materials. Hence this defect may be altered by re-processing.

Further analysis was done to seek the failure envelopes of laminates on σ_1-σ_2 and σ_2-σ_6 stress spaces. Failure envelopes were created by a simple progressive damage failure analysis done by MICMAC software offered by Stanford University. The progressive damage analysis enable the creation of predictive points on the failure envelopes out of the anchor points provided by experimental results. In the scope of this analysis, Tsai-Wu failure criterion was taken as bases in the mechanical behaviour prediction of each laminate under different loading conditions.

Figure 4.12 and 4.13 corresponds to the first ply failure envelopes of UD laminates where the competitive design space of IPCBT composite laminates was demonstrated in the shaded region.

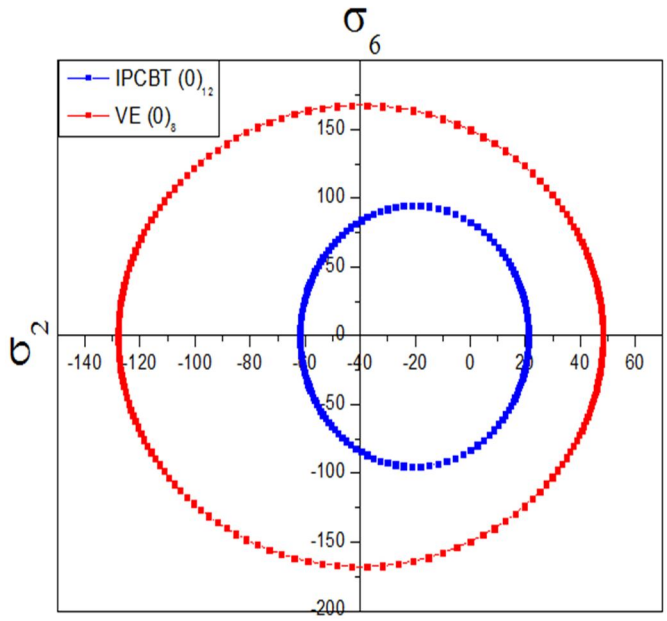


Figure 4.12 : Failure envelopes of IPCBT and VE Composites on σ_2-σ_6 spaces.

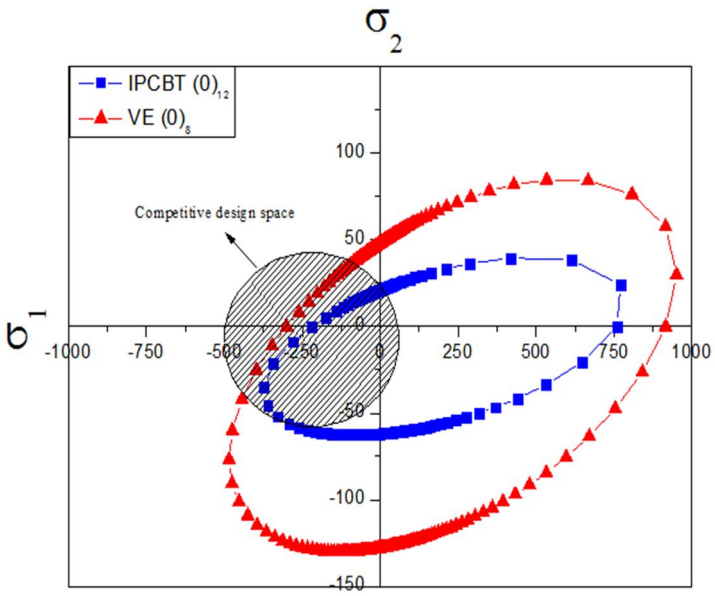


Figure 4.13 : Failure envelopes of IPCBT and VE Composites on σ_1-σ_2 spaces.

The impact strength of the biaxial IPCBT laminates was determined to be 169 kJ/m² produced with semi-isothermal, 190 kJ/m² produced with isothermal route through notched Charpy impact testing. Since there exist no published work examining the impact performance of IPCBT based composite materials, the comparison was done with respect to its thermoset equal. VE based composites having L300 coded NCGF reinforcement with a lamination sequence of (0/90)4s was manufactured by vacuum infusion and tested subsequently. The notched Charpy impact strength of biaxial VE

laminates was found to be 81 kJ/m². This remarkable difference in the impact strength can be attributed to the inherent impact absorbing capability of thermoplastics with respect to thermoset based resins.

4.3.2.2 IPCBT Composites produced with different reinforcements

The diameter of the individual filaments can be important because smaller filament diameters give higher surface area to volume ratios, which means there is more area for resin to bond to. Bonding to large area may give slightly better properties in some instances, see Section 2.2.1.3. Therefore, composite laminates were produced using X468 coded reinforcement which have smaller diameter of fibers and compared with the composites of X600 coded reinforcement which have bigger diameter of fibers. Properties of these reinforcements were explained detailed in Section 3.1.1.1. Table 4.8 summarizes tensile and flexural properties of the IPCBT composites of X600 and X468 coded reinforcements. Tensile properties show that X600 has higher tensile strength and modulus values. Higher strength and modulus of the composites with X600 can be caused by the higher strength of 600 tex fibers which have higher fiber diameter than those of 300 tex fibers since the tensile analysis gives opportunity to test more fiber dominant property. On the other hand, flexural strength of the composite with X468 resulted higher value in respect with the flexural strength of X600. Higher strength of the composite with X468 may be attributed that there is more contact between fiber and resin since the fibers with lower fiber diameter have large surface area. More contact in a large area between fiber and resin means that the resin can bond stronger on fiber surface, so this strong bond prevents the premature failure. Because the flexural properties are more composite dominant, it can be said that the reinforcement X468 which has 300 tex fibers gives better composite property when we compare with the composite including X600 in contrast the fiber property.

Table 4.8 : Comparison of mechanical properties of IPCBT composites with different fiber diameters.

Reinforcement	Fiber Diameter, µm	Max.Tensile Strength, MPa	Tensile Modulus, GPa	Max. Flexural Strength, MPa	Flexural Modulus, GPa
X600	50% of 14 50% of 15	424±11	22±1	546±7	25±1
X468	14	390±4	20±1	578±4	26±1

4.3.2.3 Production of IPCBT composites with different fiber volume fractions

An important aspect in continuous fiber reinforced composite production is to achieve the highest fiber ratio with good composite properties. This study was carried out to obtain high fiber ratio with good mechanical properties. To observe the effect of fiber content on the properties of end composite different fiber volume fractions varies between 55-65% were tried. For this purpose, the prepregs including different amounts of CBT resin were produced by compression in hot press at 200°C for 30 minutes with 1.6 MPa pressure. Produced composite parts were subjected to the tensile and impact tests. Figure A.13 (a) and Figure A.13 (b) represent tensile strength and tensile modulus variations with different volume fraction respectively. It is clear that the higher fiber ratios than approximately 63% cause significant decreasing in tensile strength and Young' modulus. Figure A.14 demonstrates impact resistances variation in different fiber volume fractions. Recorded values are nearly between 190-210 kj/m² giving not quite remarkable differences. From the micro structural point of view, it can be said that low resin volumes allow to formation of voidsa and resin poor places, which cause strength decreasing, due to the insufficient impregnation of fiber. SEM image of the composite with 63% V_f can support this assumption (See Figure A.15).

4.3.2.4 Production of IPCBT composites in different thicknesses

In order to identify influences of end laminate thickness on properties of IPCBT composites, several laminates were produced by compression in different thickness as 6 and 10 mm with X600 pre-pregs at 200°C for 30 minutes. Press load was kept in 1.6 MPa. Metal molds with 6 mm and 10 mm dept were used for the trials. For 10 mm laminates, a thin probe was placed into the centre of laminate through a drilled hole on one side of the mold to measure the temperature in the middle of the laminate during compression. Heating plates of the hot press were set up to 205°C for both upper and bottom. Figure 4.14 shows the centre temperature which the laminate reached during compression in 30 minutes. IPCBT laminates with 6mm and 10 mm thicknesses were successfully produced with a 54% fiber volume fraction.

Table 4.9 summarizes the tensile properties of IPCBT composites with different thicknesses. It can be seen that while Young' Modulus values don't change too much, tensile strength shows a decreasing. Figure A.16 (a) and A.16 (b) show SEM images of cross sectional area of the composites with 6 mm and 10 mm thickness respectively. Macro void formations between the fiber bundles can be attributed to in sufficient impregnation due to the large cross section area of composites. These

voids can give lower tensile strengths causing stress concentration which starts premature failure.

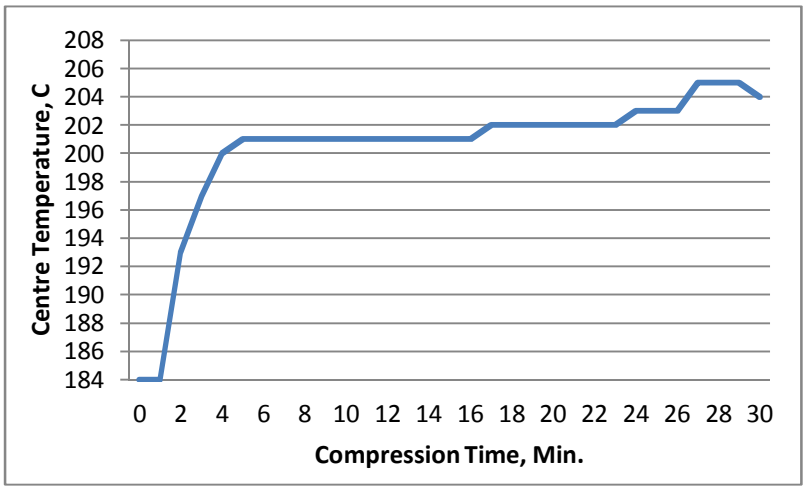


Figure 4.14 : Centre temperature of the laminate during compression molding.

Table 4.9 : Tensile properties of IPCBT composites with different laminate thicknesses.

Laminate Thickness, mm	Tensile Strength, MPa	Tensile Modulus, GPa
3	394±11	21±1
6	306±3	20±1
10	326±6	20±1

4.3.3 PA matrix composites

Nylons 6 and 12 have been used to produce thermoplastic composites through in-situ polymerisation, See Section 2.5.1. Anionic polymerisation of lactams 6 and 12 can produce nylon 6 and 12 respectively, with no byproducts, and within times acceptable to the RTM process. The drawbacks to both nylon systems include material properties and processing complications. The processing both systems are very sensitive to water and impurities (including fiber sizing) during the polymerisation process. Small amounts of water (in the few ppm range) can have adverse effects on polymerisation. There are several records on in situ polymerisation of PA matrix composites. However, some process difficulties couldn't be solved. In this section, a new method to prepare PA matrix composites is suggested. For this purpose PA matrix composites produced by suspension impregnation and powder scattering of PA 12 (see section 3.3.1.5) were analysed and compared with literature values.

Several laminates were produced with X600 and X468 coded reinforcements. The process conditions and laminate properties can be seen in Table 4.10. The pressure was hold as 3 MPa for all samples.

Table 4.10 : Process conditions and mechanical test results of X600 and X468 laminates with CoPa and PA 12 matrix.

Fabric Code	Vf, %	Number of layers	Process Time, min.	Process Temp., °C	Max. Tensile Str, MPa	Modulus, GPa	Max. Strain, %
X600	54	6	15	210	317	17	1.93
X600	54	6	15	200	-	-	-
X600	54	7	20	210	-	-	-
X468	50	8	20	210	-	-	-
X600	50	6	30	200°C for 15' 185°C in 15'	228	16	1.62

Failure of the laminates have occurred after maximum tensile strength was achieved and was differentiated by the sudden load drop observed at the end of testing, See Figure 4.15. The fracture mode of laminate can be seen in fractured test specimen image indicating sudden load drop of final fiber fracture without delamination, see Figure 4.16.

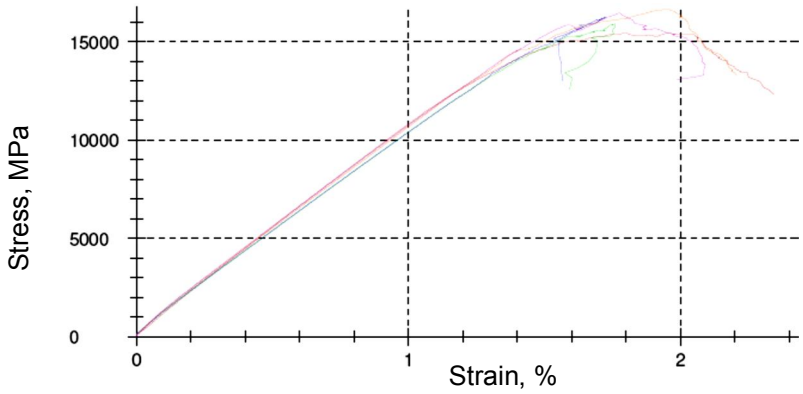


Figure 4.15 : Tensile Stress-Strain curve of PA laminates.

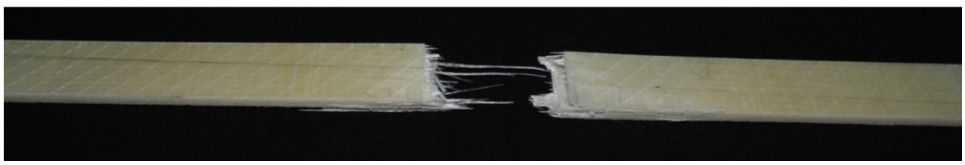


Figure 4.16 : Fractured test specimen of PA composite after tensile test.

The first problem was the marbled surface appearance, see Figure 4.17. Although first sample (Fig. 4.18) gave enough mechanical result to solve surface appearance problem, the process temperature was decreased to 200°C. Lower temperature caused worse appearance on the surface. Increasing of the number of the layers,

temperature and the time didn't improve the surface appearances. In order to improve surface and mechanical properties the idea is to hold temperature at 210°C and change the pressure for further trials.

Figure 4.17 : Marbled appearance on the surface of the composite laminate.

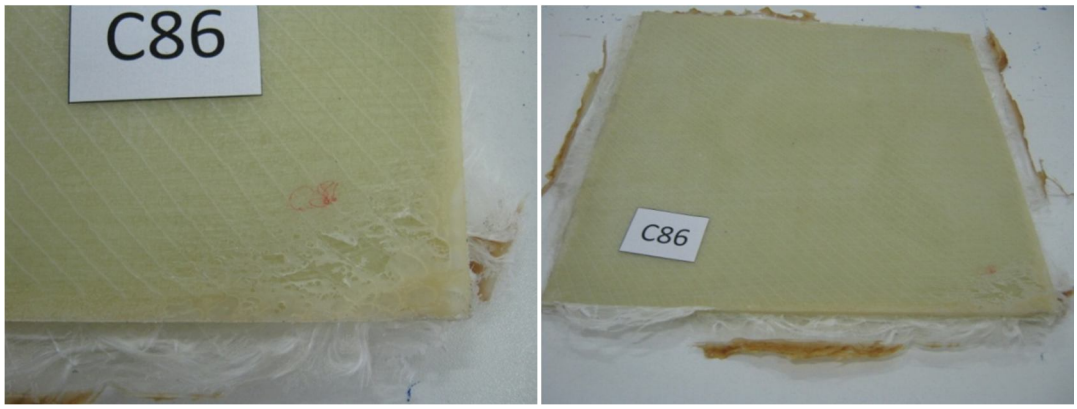


Figure 4.18 : Laminate images produced with 6 layers of X600 at 210°C for 15 minutes.

Since anionic polymerisation of PA is very sensitive to moisture, due to the nature of glass fiber many studies were done with carbon fiber. Moeginger and his co-workers reported that 390 MPa tensile strength, 26 GPa tensile modulus for glass woven reinforced anionically polymerised composite (V_f=60%) in RTM. It is clear that the tensile strength and stiffness of PA 12 composites are less than those of anionacally polymerised PA composites.

4.3.4 Composites out of commingled PBT/Glass fabric

In this section, IPCBT matrix composite was compared with the composite which has a conventional PBT matrix. PBT composites were produced by compression molding in hot press using commingled PBT/Glass fabric. Producing method has been explained in section 3.3.2 detailed. Table 4.11 summarizes the tensile

properties of IPCBT and PBT matrix composites. It can be seen that both types of PBT possess similar values of strength. However, the relatively high tensile modulus IPCBT indicates its brittle nature.

Table 4.11 : Tensile properties of IPCBT and PBT matrix composites.

Types of Matrix Used in Composite	Compression Conditions	Max. Tensile Stregth, MPa	Tensile Modulus, GPa
IPCBT	200°C, 30', 1.6 MPa Demolding @200°C	424	22
IPCBT	200°C, 30', 1.6 MPa Demolding @180°C	504	22
PBT	260°C, 30', 1.5 MPa Demolding @200°C	425	14

There are several possible reasons for this brittleness. Presence of voids, low molecular weight, high degree of crystallinity can substantially reduce the ductility of a polymeric material [19]. It was recorded that IPCBT shows much higher degree of crystallinity than commerical PBT which is polymerised by conventionally as explained in Section 2.6.1 [18, 58, 59]. Relatively low strain and low moduli of commercial PBT can be attributed to its low crystallinity when it is compared with IPCBT.

4.3.5 Production of sandwich structures with CBT and PA prepregs

There are many applications to produce structural composite sandwich laminates consisting a core material as foam of polymer etc. and fiber reinforced skins on each side of the core. Main required property in a sandwichs is the high bond strength between skin and core to have proper mechanical properties. Generally sandwichs are produced using structural adhesives such as epoxy, urethane-acrylte etc. to bond composite skins and core to each other. However, this bonding application is a second step which causes time waste in industrial scale. In this study, the purpose is to produce sandwich in one step including skin production and skin-core bonding at the same time namely called one-shot production. Therefore, core foam and several layers of prepregs were palced into metal mold in the sequence of prepregs + foam + skins then molded in hot press. CBT and PA prepregs were used as the skin and PA foam was used as core material. Before molding, PA foam was drilled, sanded and cut to make resin flow easier and increase the surface area to make bond between core and skins stronger. See Figure 4.19.

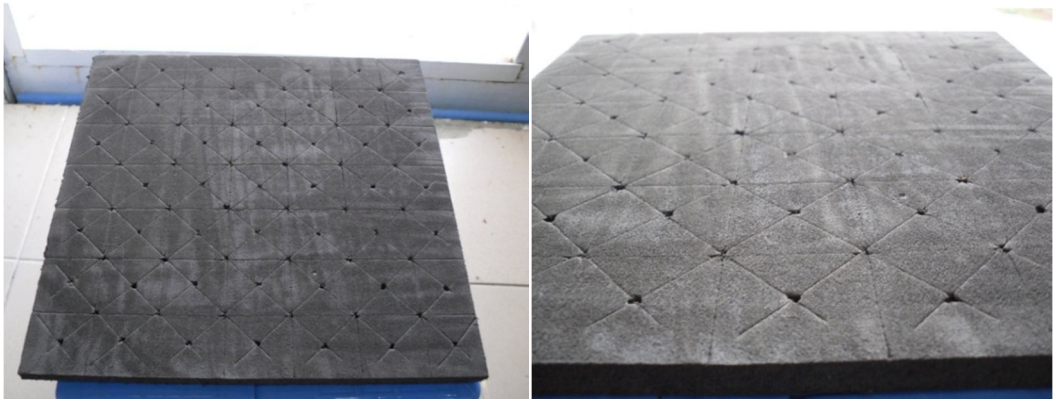


Figure 4.19 : Prepared PA foam before compression molding.

Foam was placed between 3 layers of X600-CBT prepreg on each side then into the mold with 10 mm dept, See Figure 4.20.

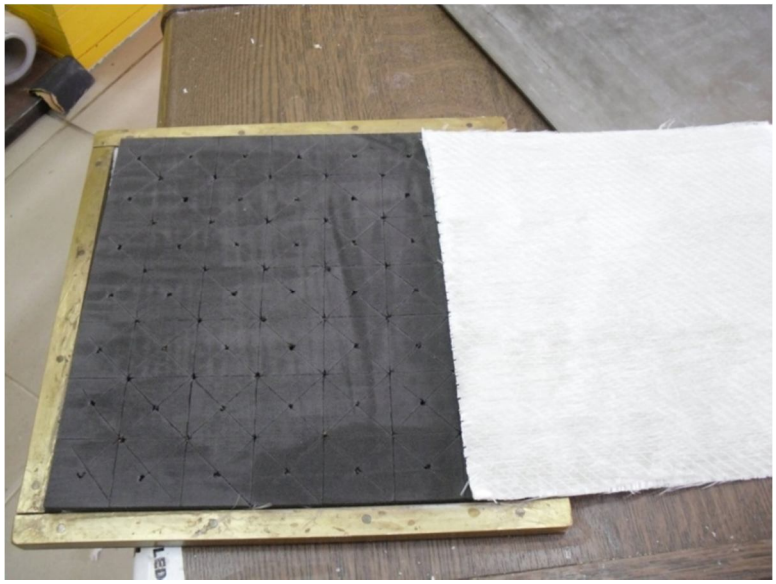


Figure 4.20 : Placement of foam and the prepregs into mold.

First trial was done with a temperature range starting from 160°C increasing to 200°C. The compression temperature, time and pressure can be observed detailed on Figure 4.21. When the system reached up to 200°C, the resin immigrated out the mold because of higher volume of the foam than the mold cavity and very low viscosity of CBT.

The best way to hold the resin in the mold was to hold pressure low until the viscosity of the resin reachs up sufficient values. Therefore, second trial was done starting with 200°C press temperature keeping the pressure as 0 MPa. Then pressure was increased at the point where the viscosity increased. Application route of this process can be seen in Figure 4.22.

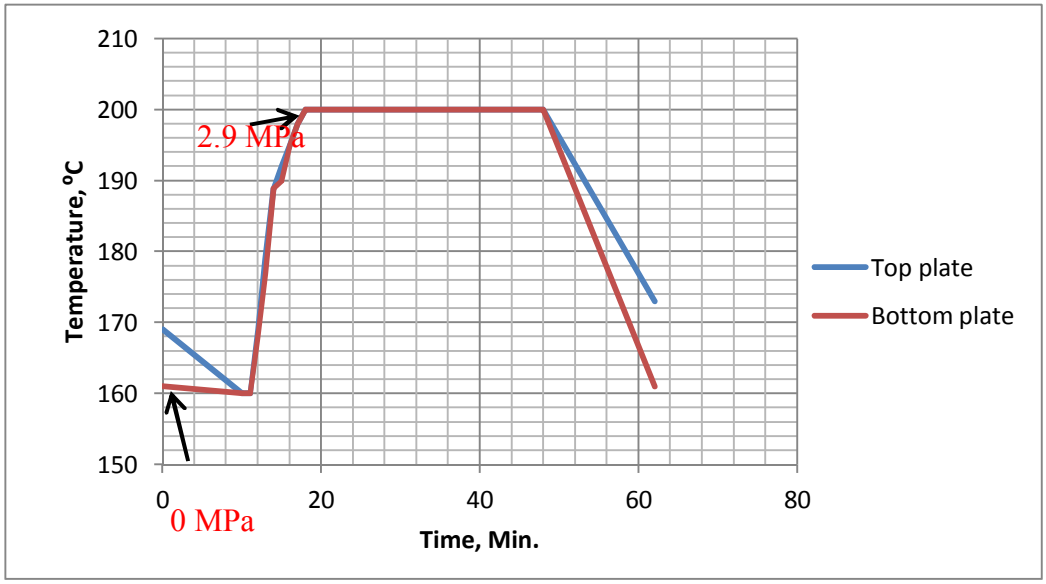


Figure 4.21 : Compression conditions for sandwich production out of CBT prepregs.

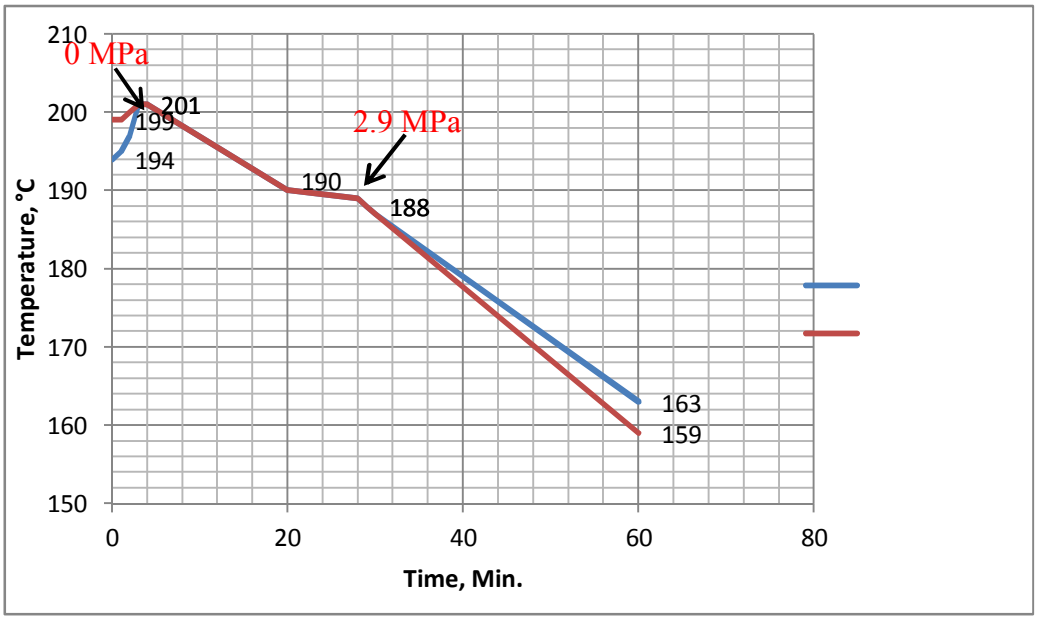


Figure 4.22 : Compression conditions for sandwich production out of CBT prepregs.

IPCBT skin PA core sandwich laminate was successfully produced by this route. See Fig. 4.23.

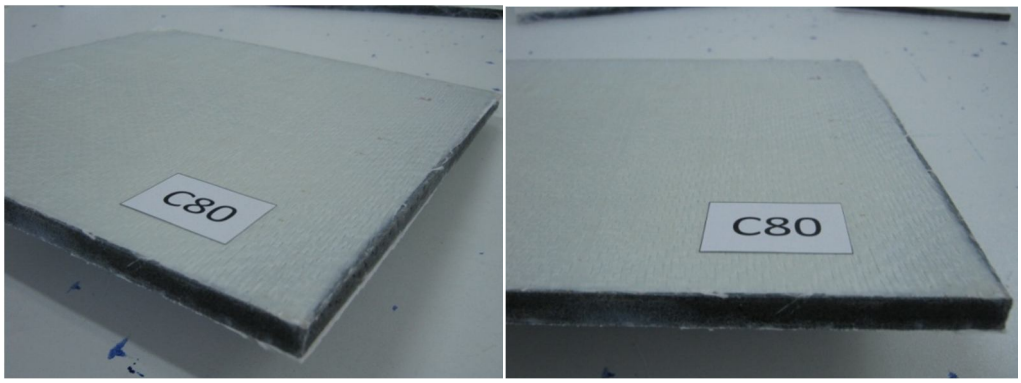


Figure 4.23 : Sandwich laminate with IPCBT skin and PA foam core.

Sandwich laminate with PA skin was produced by using 2 layers of X-600-PA prepregs and PA foam in hot press. Molding was carried out with temperature range starting from 200°C and cooling to 170°C in 25 minutes. The pressure was hold in 2.5 MPa. Sandwich laminates were successfully produced by this route, See Figure 4.24.

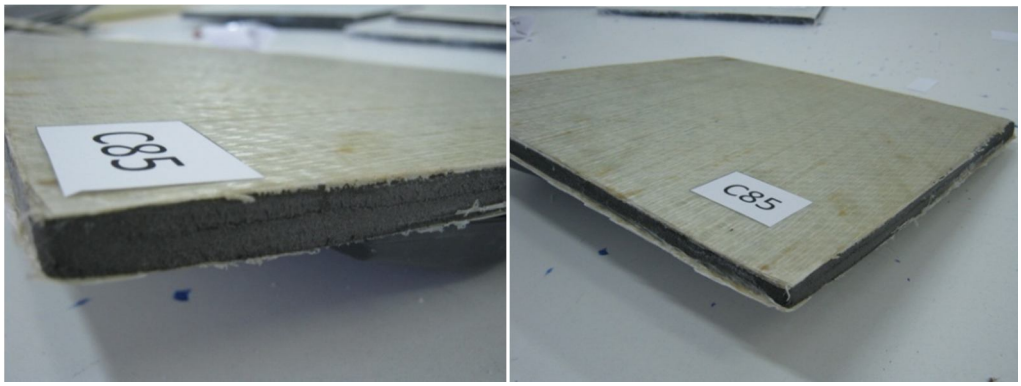


Figure 4.24 : Sandwich laminate with PA skin and PA foam core.

Bond strengths between skin and foam were measured by peeling test. Bond strength of IPCBT and PA sandwichs are 2 N/5cm, 10 N/5cm respectively. However, bond strength between skin and core was not enough for both PA and IPCBT. This low strength can be result of insufficient impregnation of foam with resin by closed cell structure of the foam. As a consequence, it is clear that the compression molding in hot press is not a proper method for one-shot TP sandwich composite production.

5. CONCLUSION AND RECOMMENDATIONS

The objective of this research is to develop a manufacturing technique for glass fiber reinforced thermoplastic matrix composites having superior properties while costs are low. This makes process and material suitable for mass production. The major purpose is mentioned in the first section.

5.1 Application of The Work

In this thesis, a new process was developed to produce NCGF reinforced PBT matrix composites. Isothermal and semi-isothermal processing of NCGF reinforced IPCBT composites via in-situ polymerisation of CBT/Glass fiber prepregs has been successfully performed by means of compression molding technique.

First of all, the prepreg production temperature which gives highest mechanical property was identified as 160°C. The optimum compression parameters which give highest mechanical properties were identified as 200°C compression temperature, 30 minutes compression time and 1.6 MPa compression pressure for isothermal process. Semi-isothermal process with 180°C demolding temperature gives higher tensile and flexural properties than isothermal process. However, impact strength of IPCBT composite produced with isothermal process is higher than that of the composites produced with semi-isothermal process. Although preimpregnation at temperatures below 200°C during compression slightly increases flexural strength, longer process period and energy lost make this route useless. It is also concluded that IPCBT composites can be produced not only by compression molding but also vacuum molding with a strength enhancement for both tensile and flexural.

Biaxial NCGF reinforced IPCBT composites gave better flexural and tensile properties when it was compared with reported results of IPCBT composites produced by RTM technique and the composites produced by compression molding of Glass/PBT commingled woven fabric in the literature. SEM analysis revealed that there is good interfacial bonding between IPCBT matrix and NCGF. If more so, the micro void formation, probably caused by trapped air during compression, was reduced in respect of the composites produced by RTM. Thus, it can be concluded

that the decreased distance between resin and fiber surface by pre-impregnation before compression process, which is namely called prepreg, facilitates good penetration of the resin through inner fibers. Moreover, if the processing time of RTM technique is taken into account, the processing time can be reduced eliminating resin-catalyst heating and mixing period with prepreg compression method proposed. Moreover, suggested method eliminates the narrow impregnation time problem which can cause uncomplete impregnation resulting dry fibers in RTM system. For the composite production out of conventional PBT/Glass commingled fibers, it can be said that the higher process temperatures and cooling necessity during the compression molding of commingled fabric shows the advantages of suggested method in this study reducing time and cost and increasing wetting ability of the fibers. Comparison of IPCBT composites and PBT composites out of commingled PBT/Glass fibers showed that while the tensile strength doesn't change, IPCBT matrix has higher stiffness with high tensile modulus. It must be considered that PBT matrix composites can be produced at temperatures which is higher than 250°C and, isothermal process is not possible.

Additionally, a detailed mechanical testing effort was done on the unidirectional laminates of IPCBT and was consecutively discussed with vinyl ester based laminates. Investigation of the test results and failure modes in accordance with the failure envelopes suggested that the IPCBT based laminates considered in this study can be strong alternatives to the VE based laminates especially under uniaxial compressive loading conditions as well as impact loadings. However, the performance of UD IPCBT laminates was found to be lower under tensile and in-plane shear modes due to high susceptibility to matrix crack formation.

In the literature, the composites fiber reinforced, sizing removed by burning off fiber reinforced and without fiber were produced using IPCBT as the matrix by RTM and hot press processes. In these studies, changing of molecular weight of IPCBT matrix with used processes and the applied temperatures were also investigated. It was found that, the achieved molecular weights with RTM at 190°C and 230°C are Mw=85 kg/mol Mn=39 kg/mol, and Mw=73 kg/mol Mn=35 kg/mol respectively. Recorded molecular weights with hot press are Mw=78 kg/mol Mn=34 kg/mol for 190°C, Mw=79 kg/mol Mn=36 kg/mol for 240°C. According to the results it is clear that process type and process temperature do not affect significantly molecular weight of IPCBT [20, 23].

PA matrix composites were successfully produced by compression molding as well. IPCBT composites gave higher tensile properties when they were compared with each other.

Sandwich structures of IPCBT and PA skin using PA foam were successfully produced. However, bond strength between skin and core was not enough for both PA and IPCBT. It was concluded that the compression molding in hot press is not a proper method for one-shot sandwich composite production.

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APPENDICES

APPENDIX A : FIGURES OF EXPERIMENTAL RESULTS

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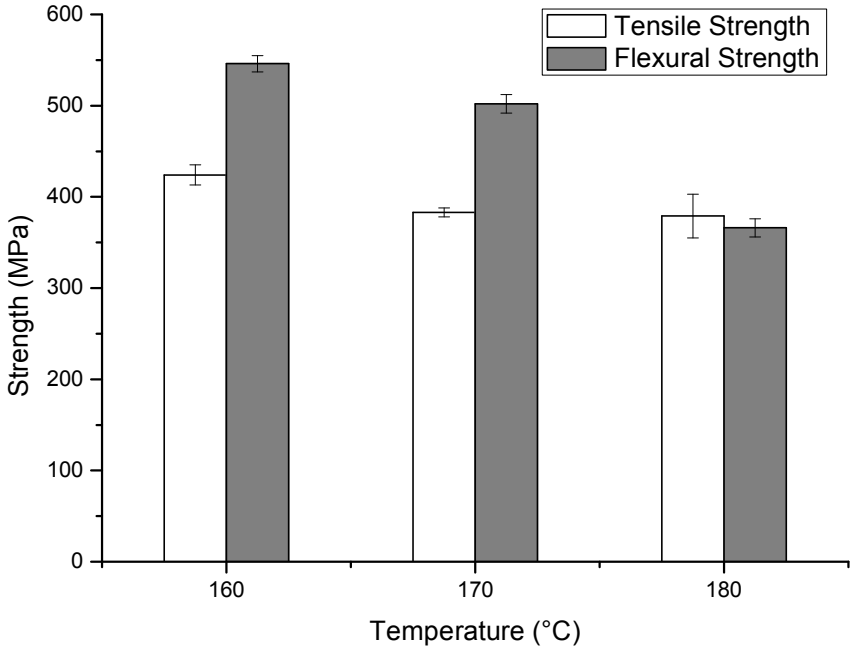

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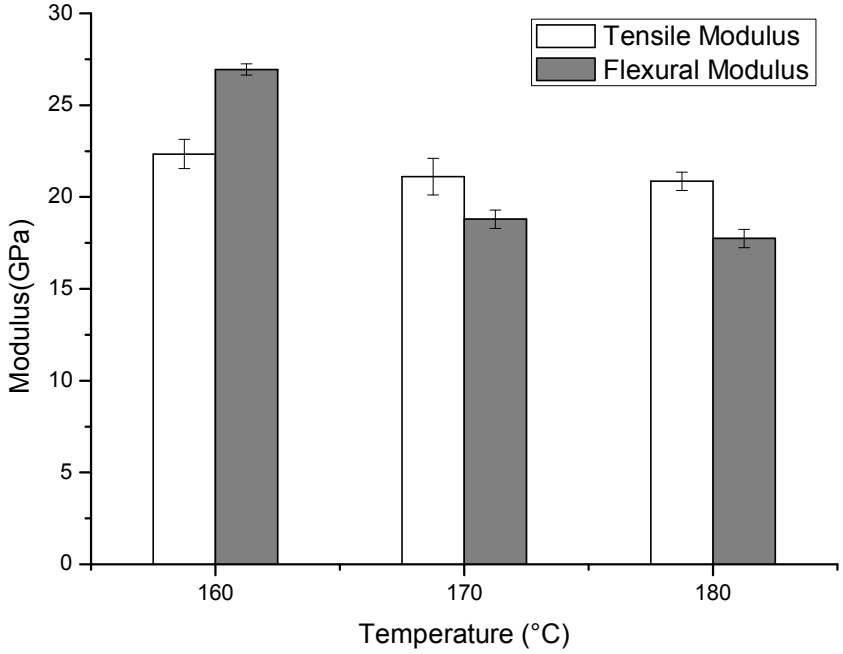
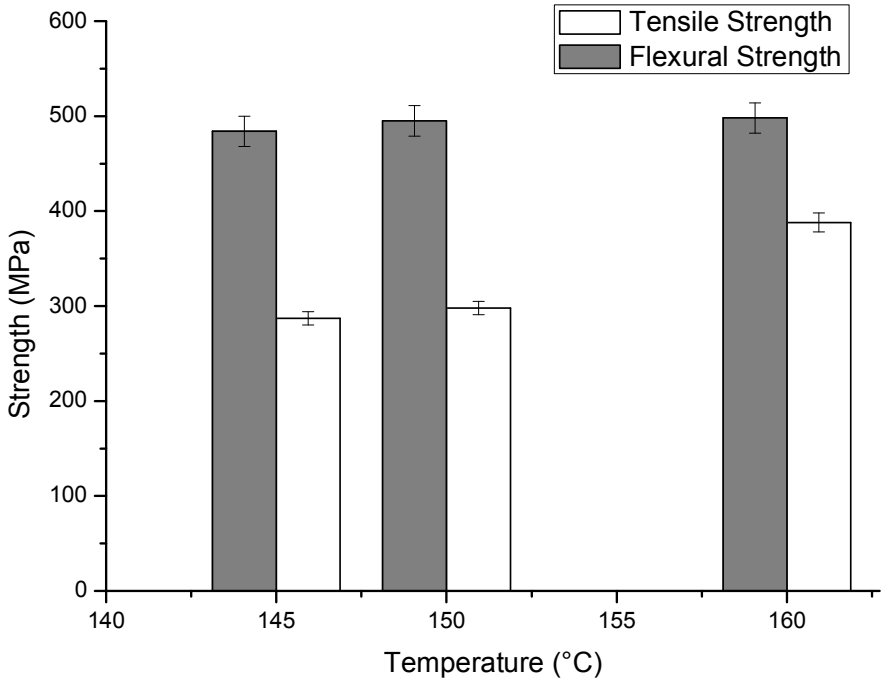


(b)

Figure A.1 : Tensile and flexural properties of IPCBTs: Hand scattering temperature.



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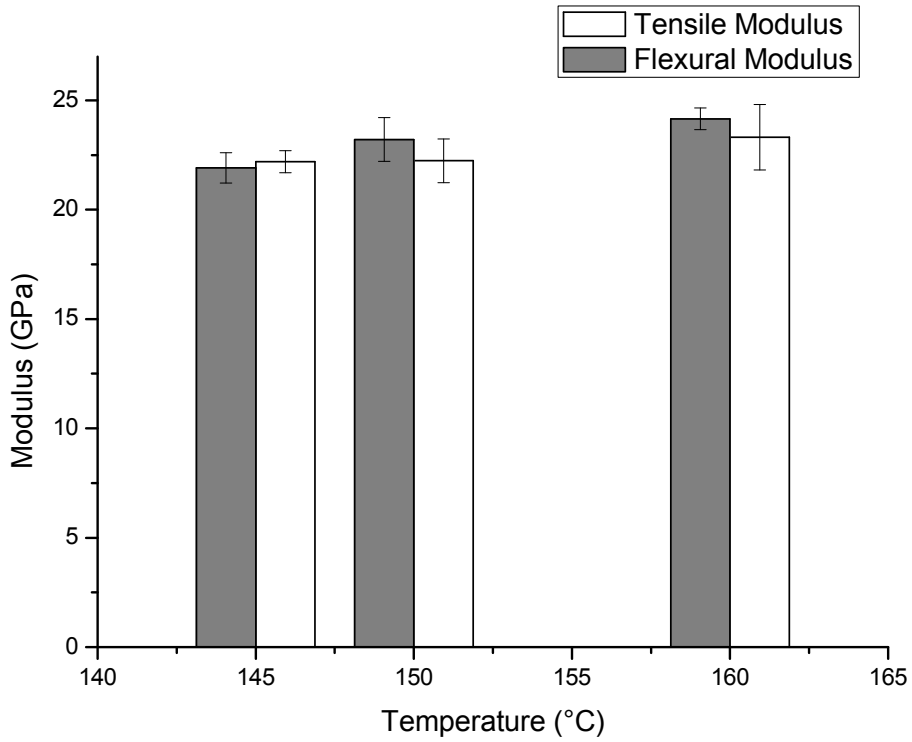
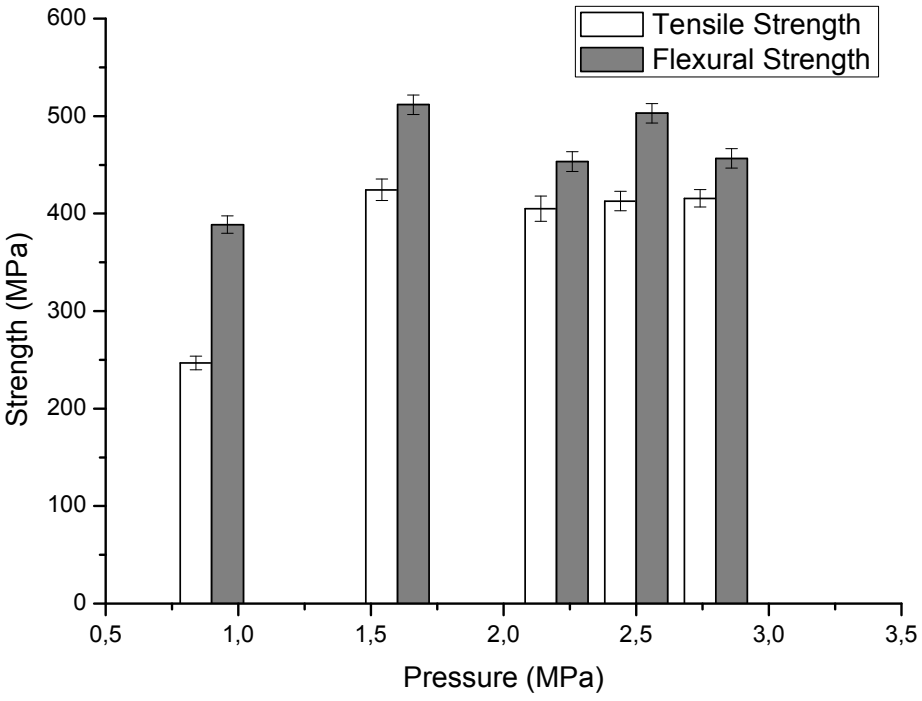


(b)

Figure A.2 : Tensile and flexural properties of IPCBTs: Scattering coating temperature.



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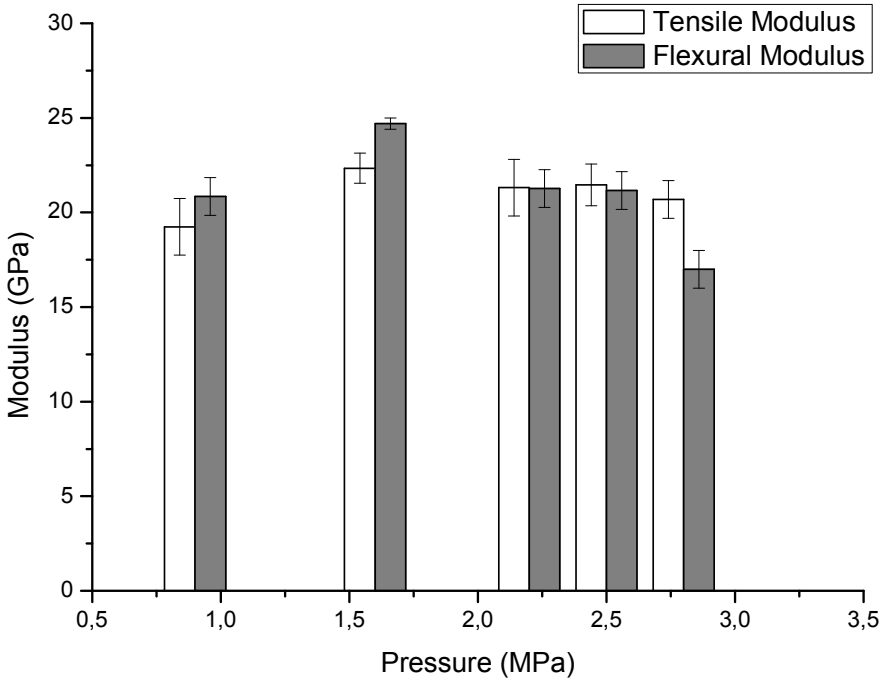
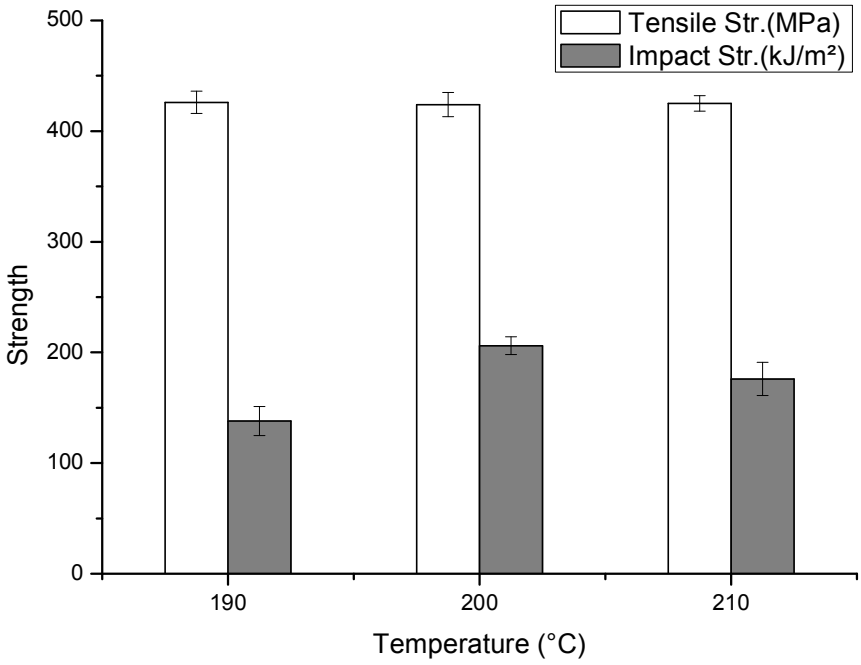


(b)

Figure A.3 : Tensile and flexural properties of IPCBTs: Compression molding pressure.



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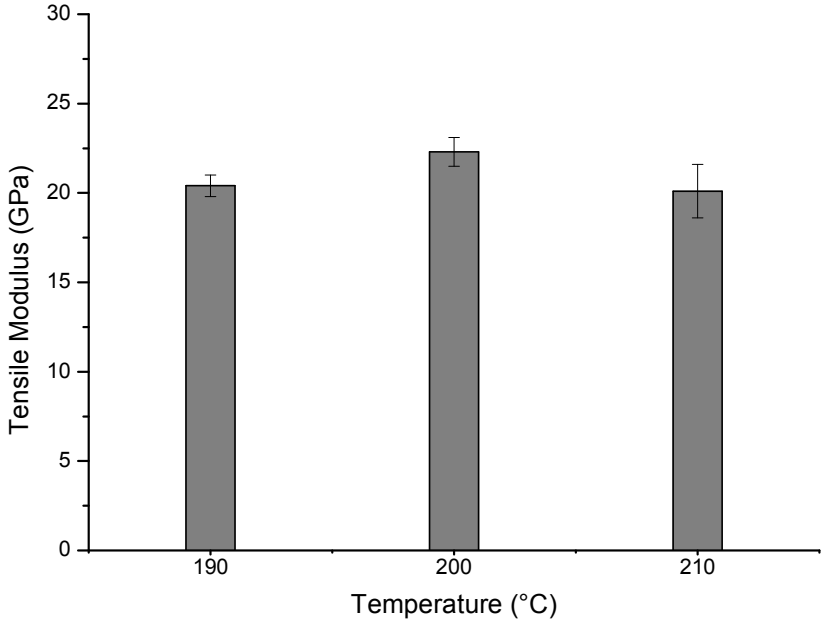
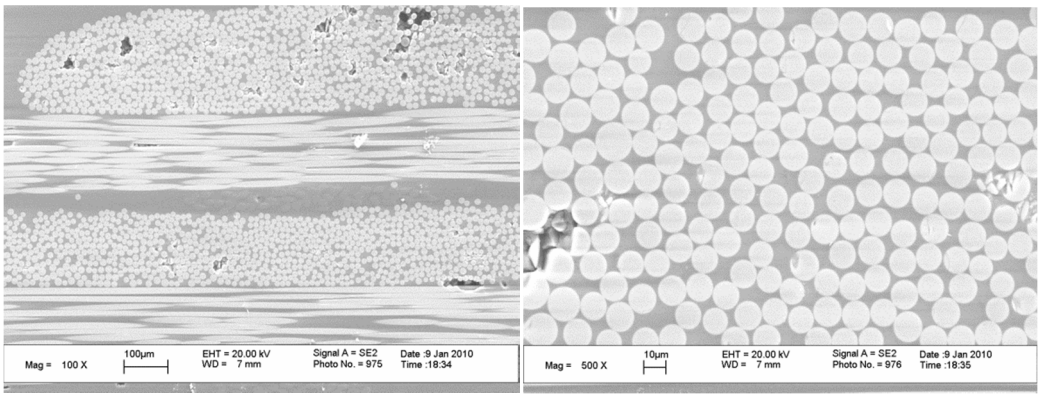


(b)

Figure A.4 : Tensile and impact properties of IPCBT composites: Compression molding temperature.



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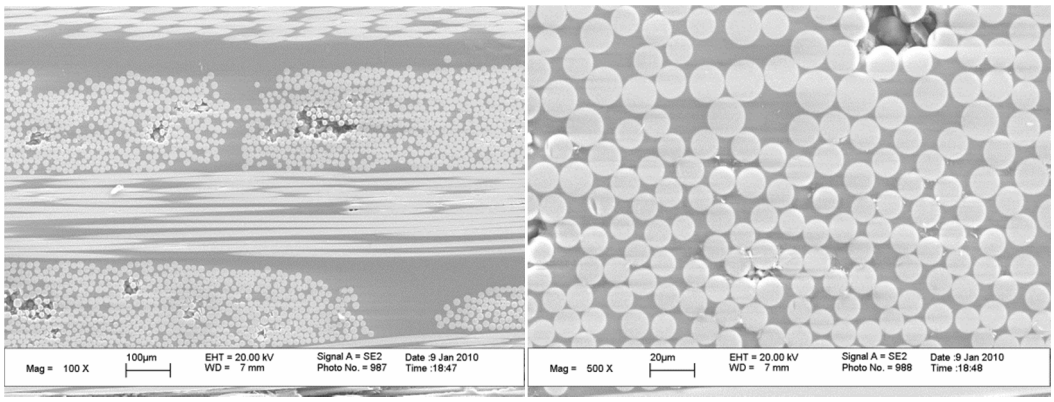

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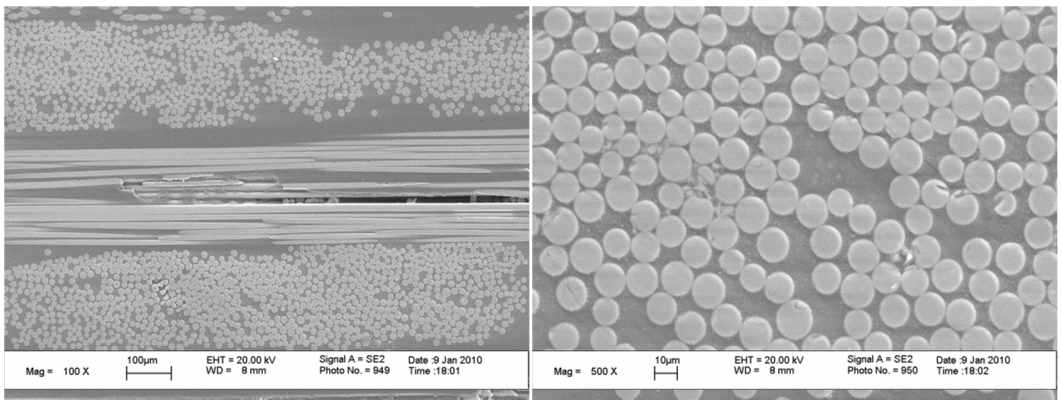
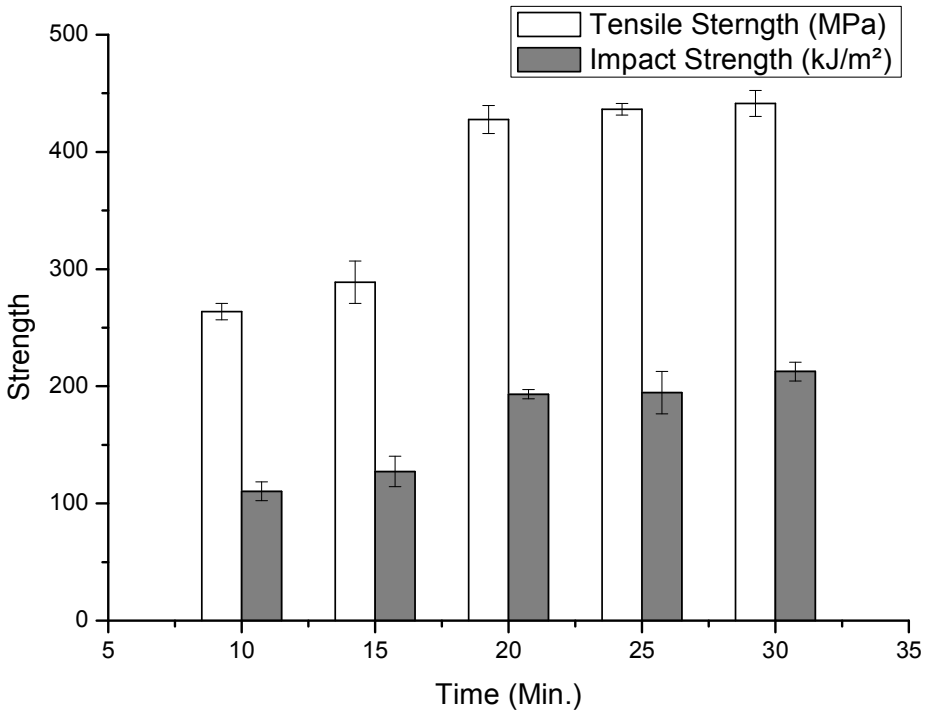


(c)

Figure A.5 : SEM images of IPCBT composites with different compression temperatures: a)210°C, b)200°C, c)190°C.



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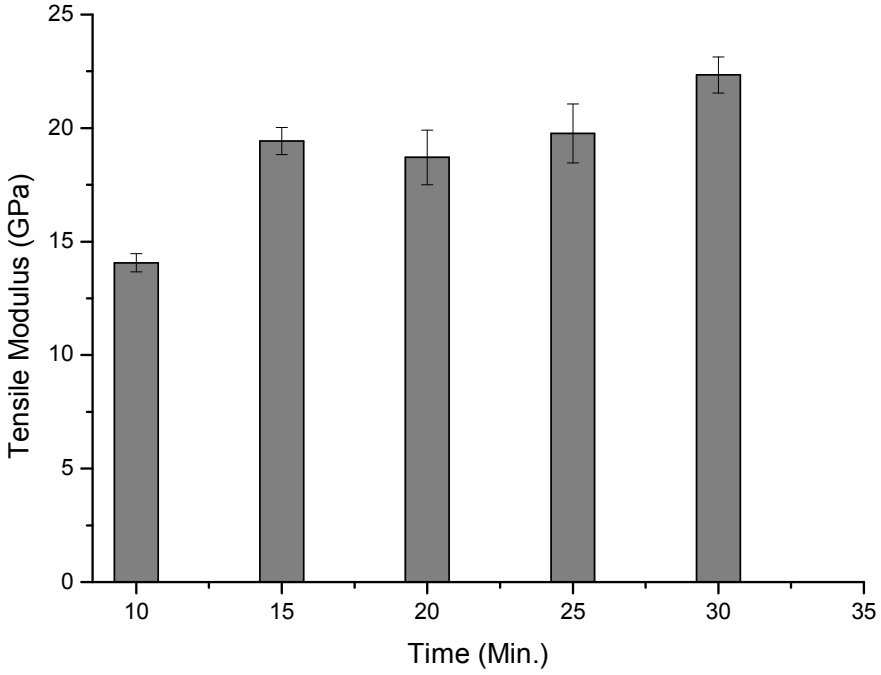
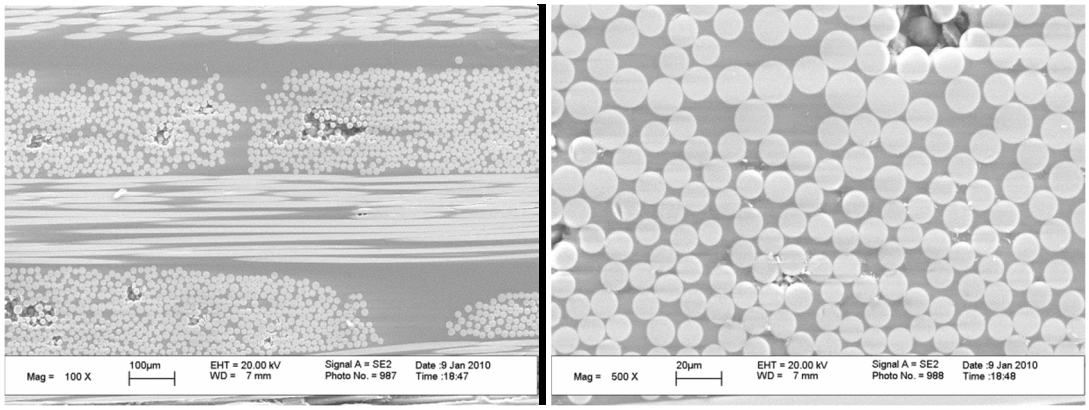


(b)

Figure A.6 : Tensile and impact properties of IPCBTs with differerent compression time.



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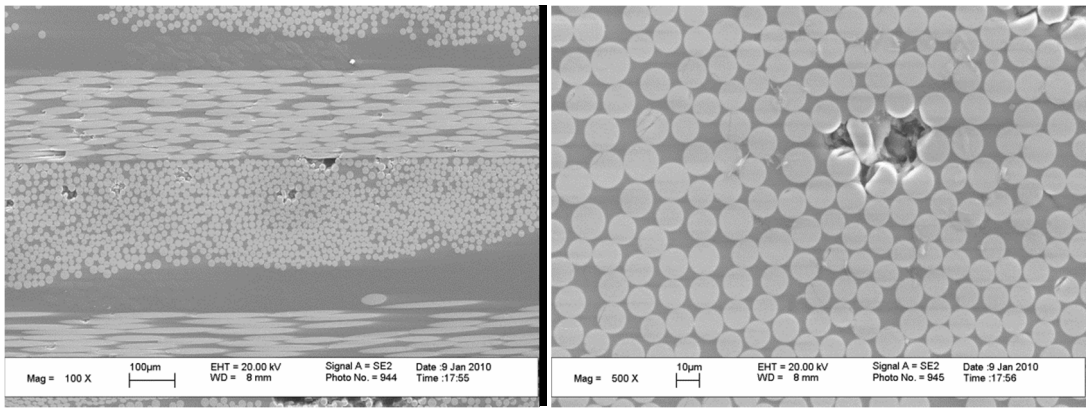
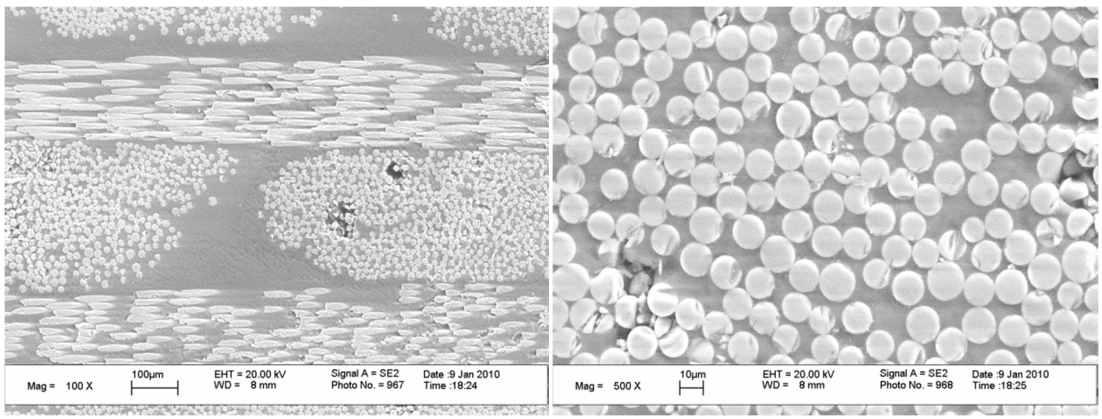


(b)



(c)

Figure A.7 : SEM images of IBT composites with different compression time: a)30', b)20', c)10'.

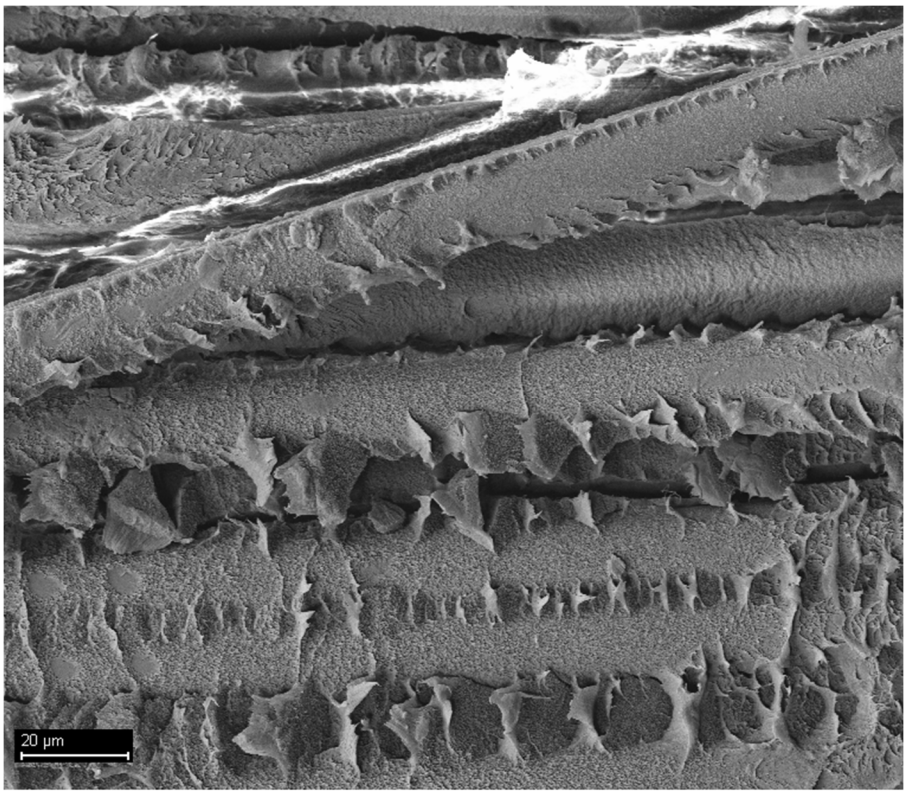
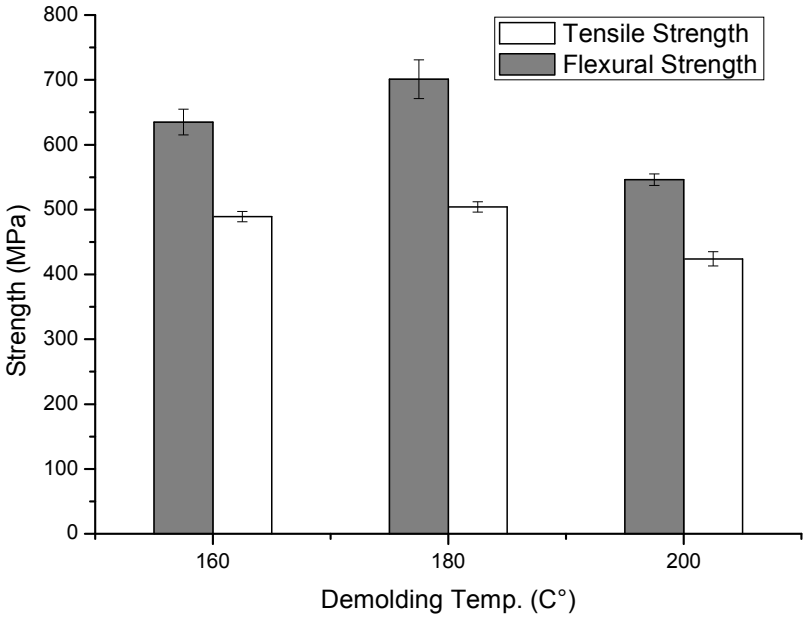
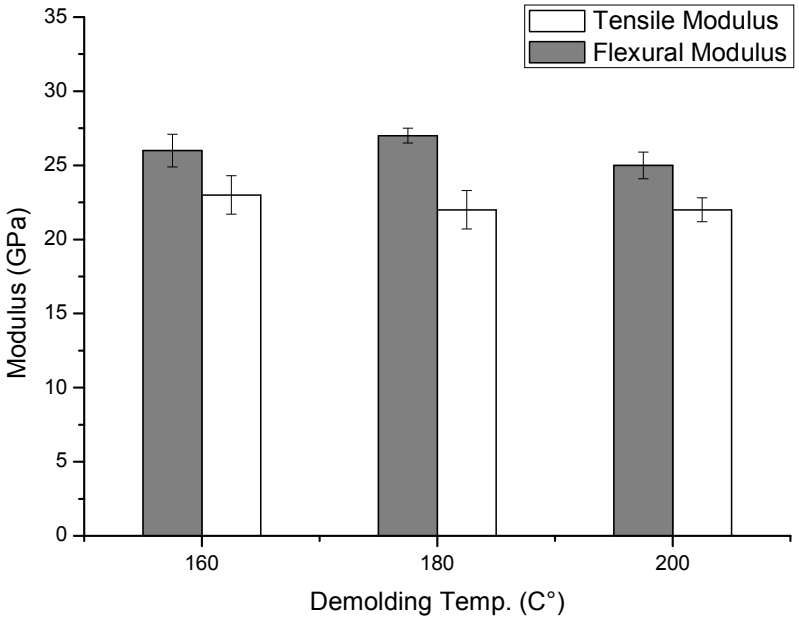


Figure A.8 : SEM image of the peeled surface of IPCBT composite laminate.

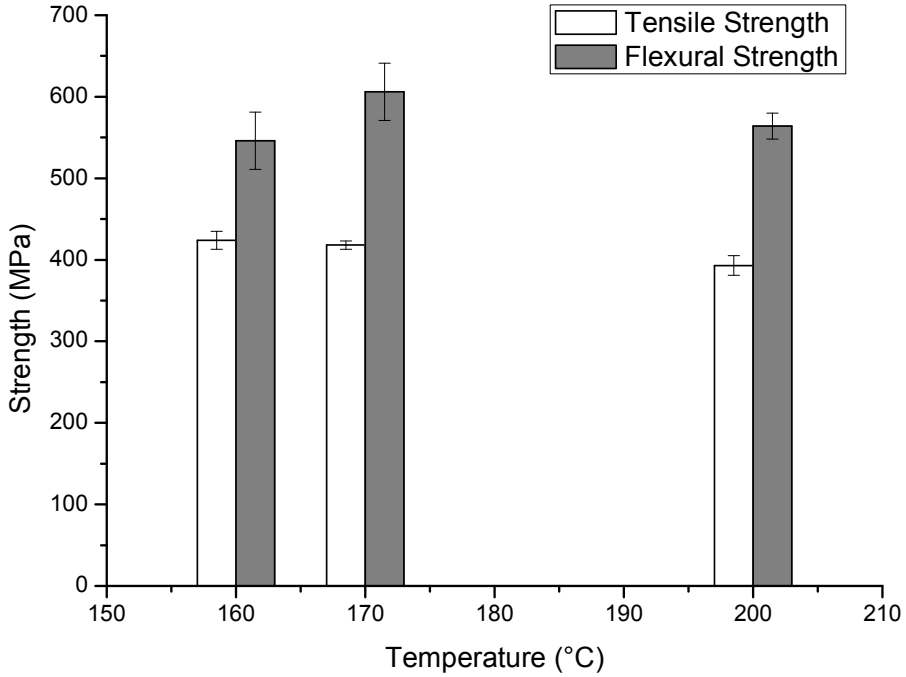


(a)

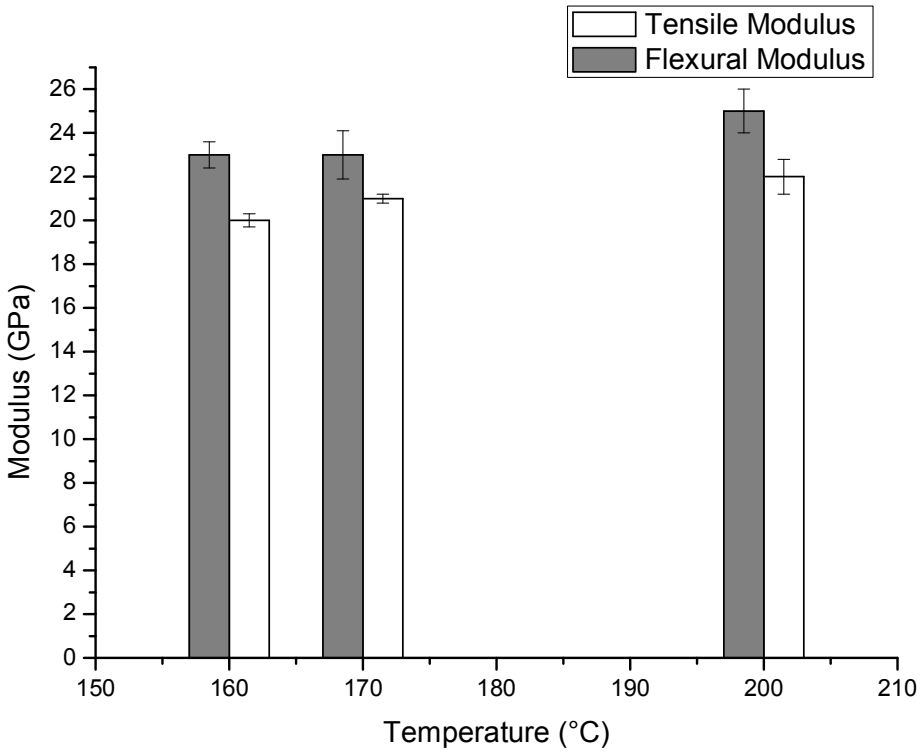


(b)

Figure A.9 : Tensile and flexural properties of IPCBT composites with different demolding temperatures.

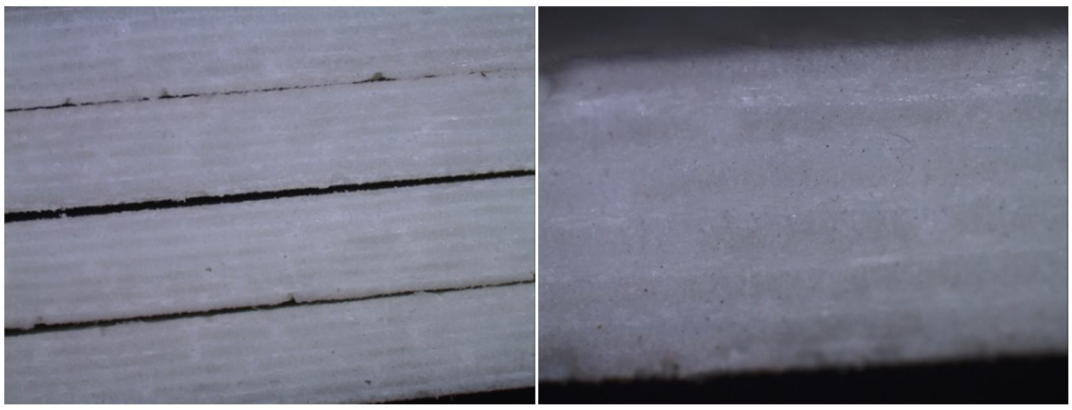


(a)

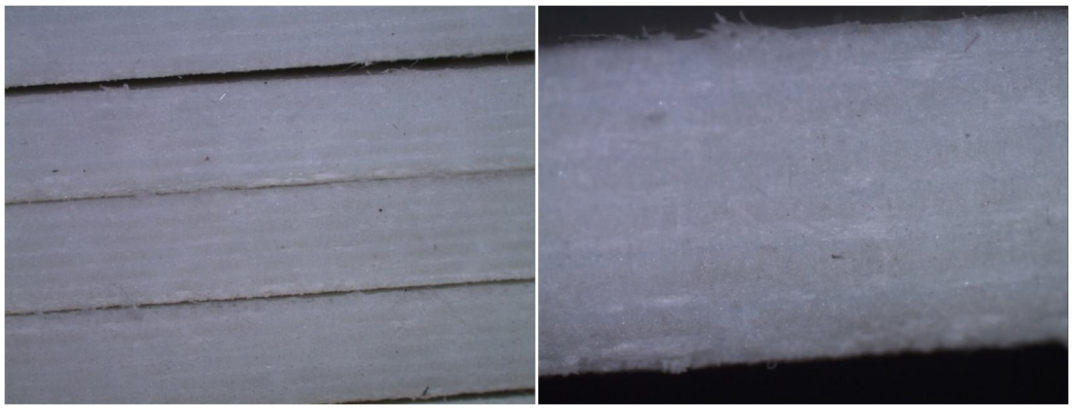


(b)

Figure A.10 : Tensile and flexural properties of IPCBT composites with different process cycles.



(a)



(b)

Figure A.11 : Stereo microscope images of IPCBT composites produced with different preimpregnation temperatures: a) 160°C b)170°C.

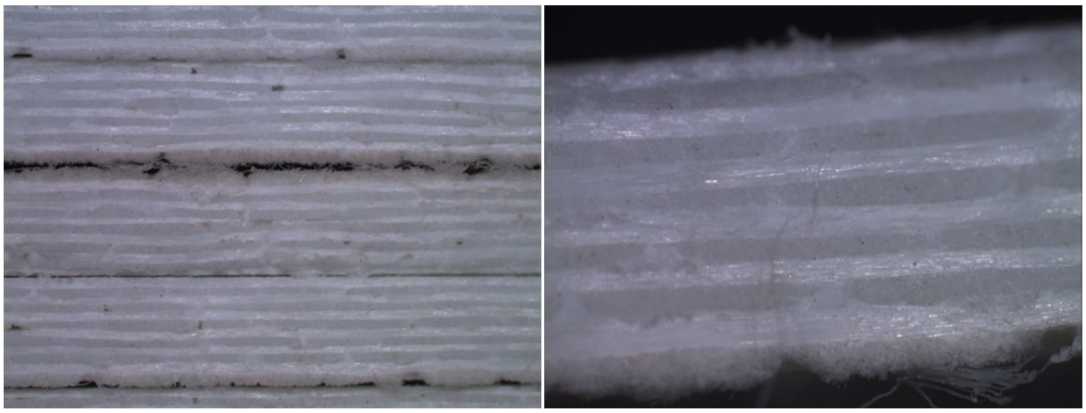
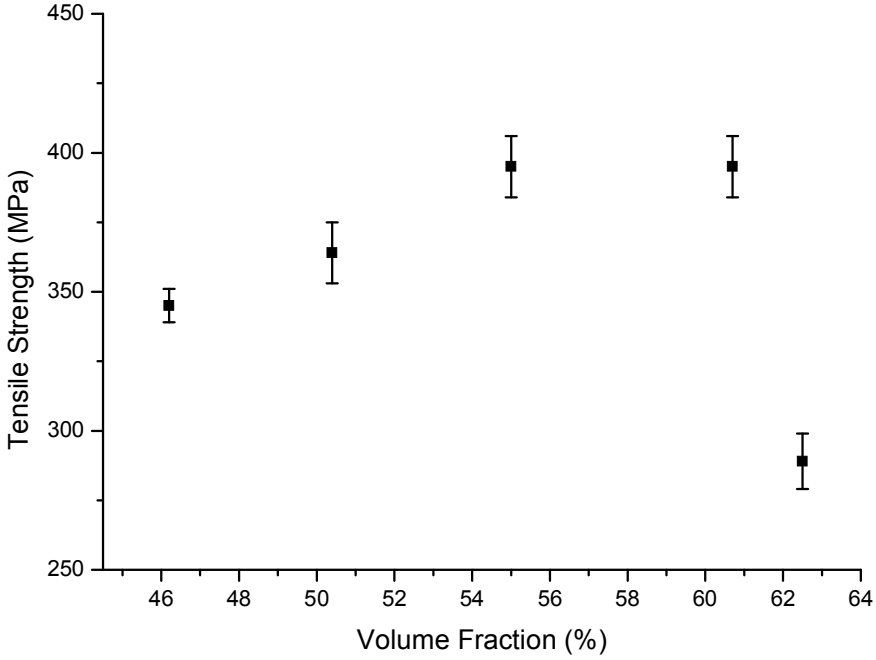
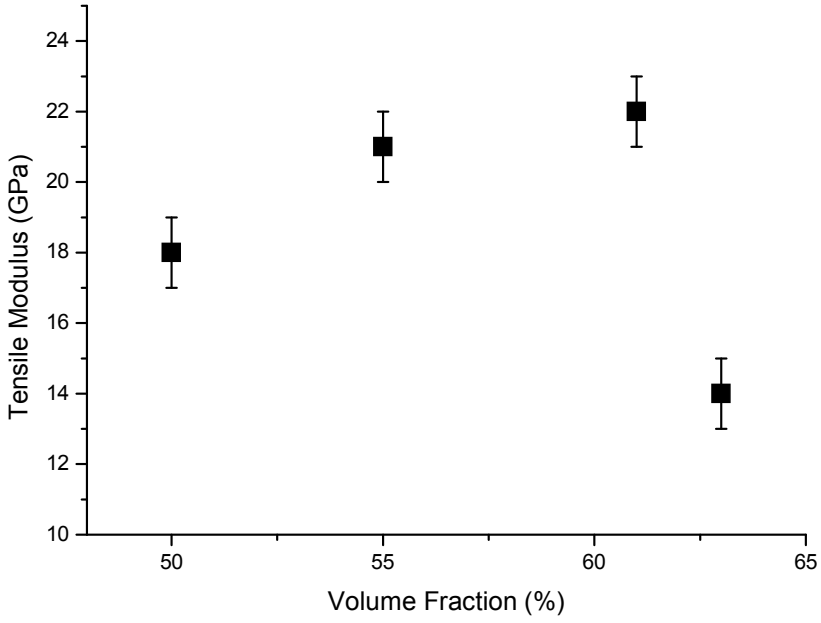


Figure A.12 : Stereo microscope images of IPCBT composite produced with 160°C preimpregnation temperature for 20 minutes compression time.



(a)



(b)

Figure A.13 : Tensile strength and tensile modulus variations of IPCBT composites with different volume fractions.

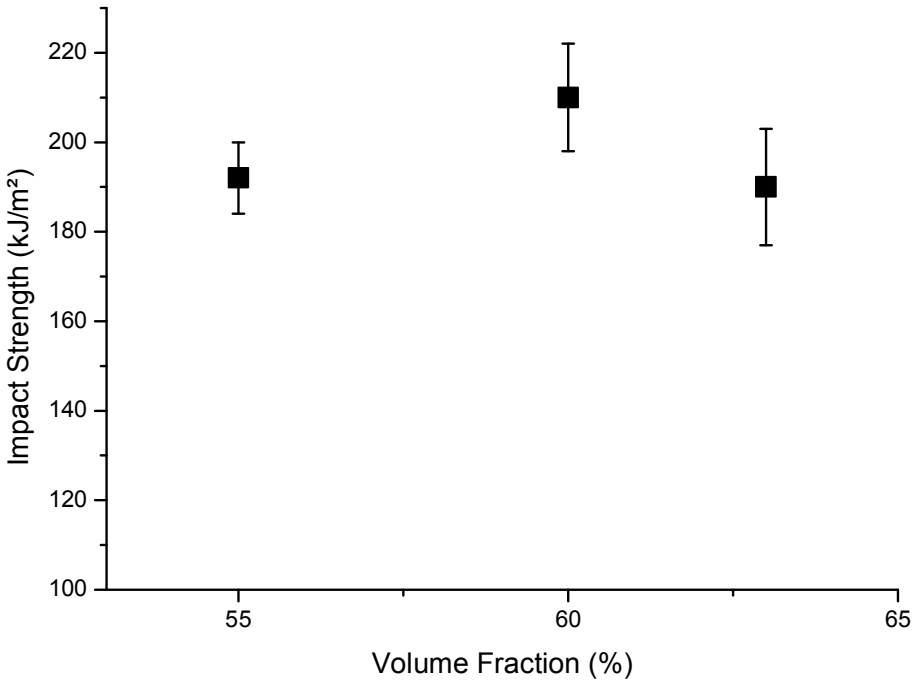


Figure A.14 : Impact strength variation of IPCBT composites with different volume fractions.

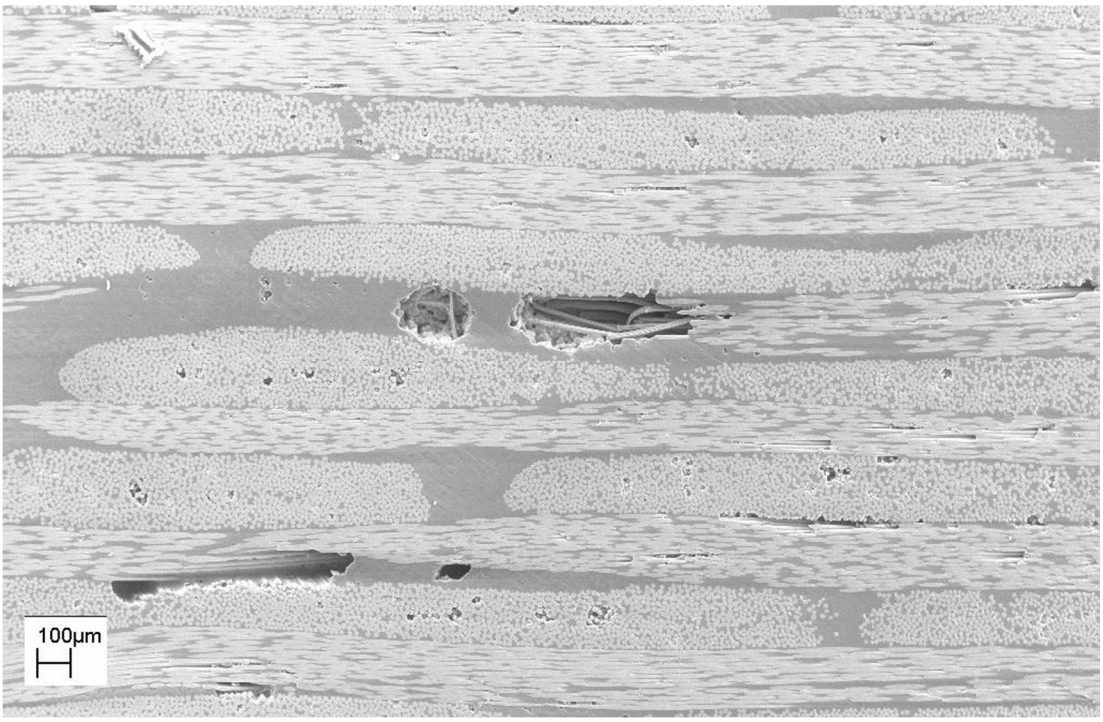
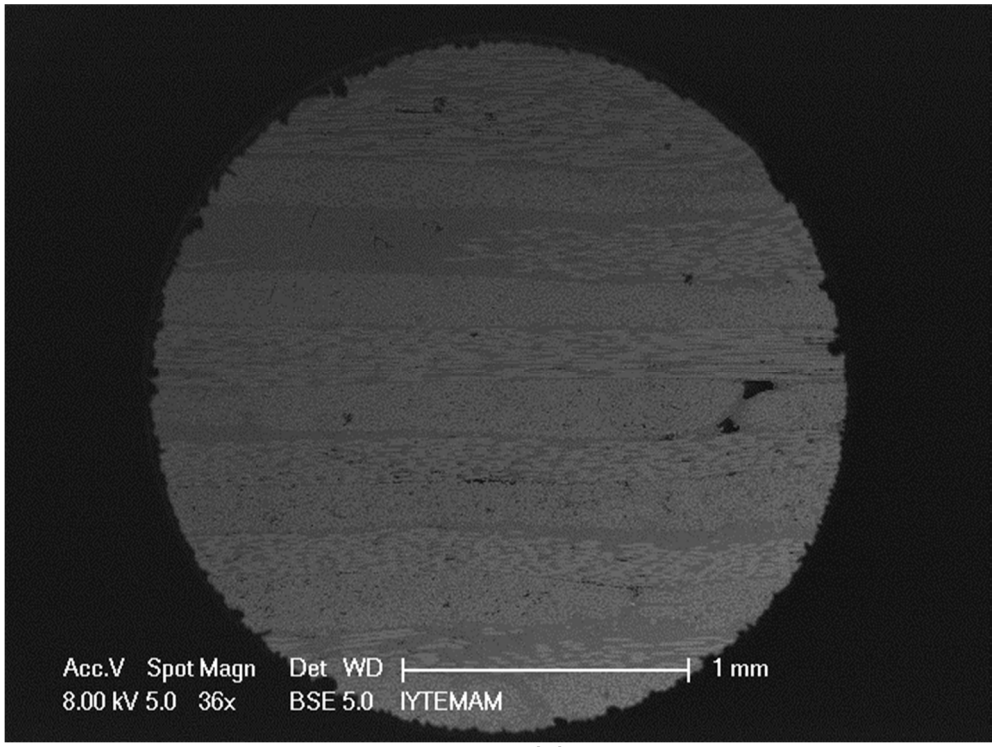
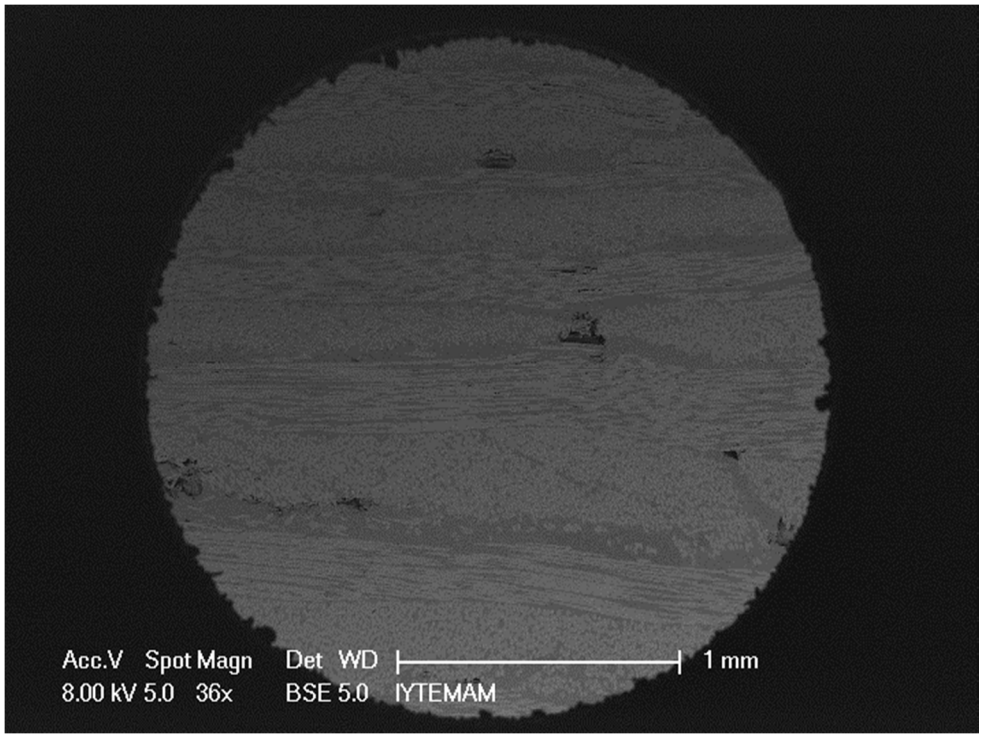


Figure A.15 : SEM Image of cross sectional area of IPCBT composite (Vf: 63%).



(a)



(b)

Figure A.16 : SEM images of cross sectional area of the composites with 6 mm(a) and 10 mm(b) thickness.

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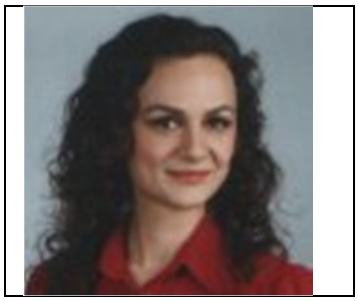

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Publications:

- **Başer, G.**, Bilge, K., Papila, M., Uyanık, N. 2012: Investigation of the strength and failure envelopes of non-crimp glass fiber reinforced thermoplastic composites based on in-situ polymerized cyclic oligomers*. ECCM15-15*th *European Conference On Composite Materials Congress June 24-28, 2012 Venice, Italy*.

- **Başer, G.**, Uyanık, N. 2010: Manufacturing of multiaxial non-crimp form glass fiber reinforced thermoplastic composites. *PPS-26 Regional Meeting, 20–24 October, Istanbul, 2010, Turkey.*

- **Başer, G.**, Uyanık, N. 2010: Multiaxial continuous glass fiber reinforced thermoplastik composites manufacturing. *National Polymer Science and Technology Congress, May 12, 2010, Kocaeli, Turkey.*

- **Başer, G.**, Uyanık, N. 2010: Thermal and rheological characterization of polyolefin compatibilizers grafted with itaconic acid and its monoesters for nanocomposites. *ECCM14-14th European Conference On Composite Materials, June 7-10, 2010 Budapest, Hungary.*

- **Başer, G.**, Uyanık, N., Eriman, B. 2006: Itakonik asit monoesterleri ile polietilen aşı kopolimerlerinin sentezi, karakterizasyonları ve teorik olarak incelenmesi. *XX. National Chemistry Congress*, September 4-8, 2006, Kayseri, Turkey.

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